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Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP (National Acid Precipitation Assessment Program) Emission Inventory

GCA Corp., Chapel Hill, NC

Prepared for

Environmental Protection Agency
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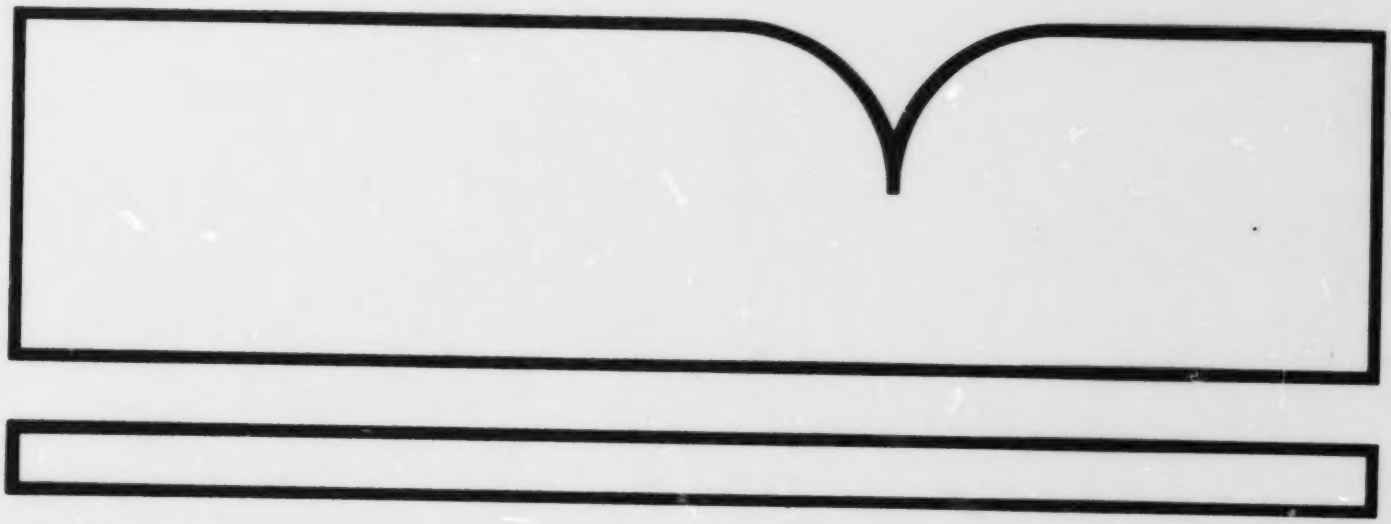

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16. ABSTRACT The report gives results of a study to develop emission factors for significant sources of hydrogen chloride and hydrogen fluoride. Information developed in the report includes significant emission sources, source descriptions, uncontrolled emission factors, controls commonly used, and average control efficiencies. An assessment of the accuracy of each efficiency factor is also included.

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HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE EMISSION FACTORS FOR THE NAPAP EMISSION INVENTORY

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ABSTRACT

The National Acid Precipitation Assessment Program (NAPAP) has determined that estimates of hydrogen chloride and hydrogen fluoride are needed in its emission inventory. In this study, sources of emissions to the atmosphere of hydrogen chloride and hydrogen fluoride were identified and associated emission factors were estimated. Emission factors were based on the most recent data available and were used to develop nationwide emission estimates for base year 1980. Descriptions of each source category, controls commonly used for each emission source, and an assessment of the accuracy of each emission factor are also included. Major sources of hydrogen chloride are coal combustion, public refuse incineration, and organic chemical manufacture. Approximately 660,000 tons/year of hydrogen chloride were emitted in 1980; over 89 percent of the total resulted from coal combustion. Hydrogen fluoride was emitted from various sources at the rate of 90,000 tons/year. Coal combustion, comprising 78 percent of the total, and primary aluminum production, comprising almost 15 percent, are the major hydrogen fluoride sources. Other sources include the fertilizer industry and the hydrogen fluoride manufacturing industry.

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The Appendix was prepared by Mark Gollands, Bob Kane, Sean O'Brien and Tom Sylvia of GCA Corporation under the supervision of EPA Project Officer Merrill D. Jackson (EPA Contract No. 68-02-3698, Task No. 2). The report has been reviewed and approved for publication by appropriate EPA and NAPAP personnel.

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SECTION 1
EXECUTIVE SUMMARY

The focus of emission inventory activities within the National Acid Precipitation Assessment Program (NAPAP) is to estimate emissions of pollutants of concern to the acid deposition phenomenon. While sulfuric and nitric acids are considered primary precursors of acid deposition, contributions of hydrogen chloride (HCl) and hydrogen fluoride (HF) are also significant. This report presents emission factors for HCl and HF from significant sources of these pollutants.

A literature search was conducted to identify significant anthropogenic emission sources and estimate emission rates for each source. The emission factors summarized in Table 1-1 were developed from the most recent data available. When available, emission factors based on tests performed by a sound methodology and accompanied by adequate background data were chosen. Emission factors were evaluated on a scale of A through E with an A representing data from a large data base covering a good cross section of the industry, determined from valid test methods, and with a high confidence level. Data rated E were developed from a small data base, not necessarily representative of the industry, and with a low confidence level. Ratings of B through D represent data with intermediate confidence levels. National emission estimates for base year 1980 were calculated by multiplying the level of activity (production/use rates) for each source category in 1980 (or as close to base year 1980 as possible) by the emission factor for that source. National emission estimates provide a measure of the relative importance of each source category.

Hydrogen chloride is emitted from coal combustion, waste incineration, and organic chemical manufacture. Approximately 660,000 tons of hydrogen chloride were emitted in 1980; over 89 percent of the total resulted from coal combustion. Hydrogen fluoride was emitted from various sources at the rate of 90,000 tons/year. Coal combustion, comprising 78 percent of the

TABLE 1-1. EMISSIONS OF HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE

Source	Emission factor[a]	Emissions (tons/yr)	Emission factor accuracy rating
	-- HCl--		
Coal Combustion			
Utility Boilers			
Bituminous	78.8 lb/10^9 Btu	458,200	A
Anthracite	35.5 lb/10^9 Btu	310	A
Lignite	1.0 lb/10^9 Btu	270	A
Industrial Boilers			
Bituminous	78.8 lb/10^9 Btu	121,000	A
Anthracite	35.5 lb/10^9 Btu	530	A
Lignite	1.0 lb/10^9 Btu	40	A
Residential Boilers			
Bituminous	60.5 lb/10^9 Btu	1,300	C
Anthracite	120 lb/10^9 Btu	1,300	C
Lignite	35.1 lb/10^9 Btu	--	C
Propylene Oxide Manufacture	7.46 lb/ton	2,140	B
Incineration			
Municipal Waste	5.0 lb/ton[b]	75,000	E
Industrial Waste	5.35 lb/ton[b]	--	E
Liquid Waste	1.19 lb/ton[b]	--	E
By-product Hydrochloric Acid Production			
(without final scrubber)	3.0 lb/ton	--	C
(with final scrubber)	0.2 lb/ton	--	C
	--HF--		
Coal Combustion			
Utility Boilers			
Bituminous	9.4 lb/10^9 Btu	54,670	A
Anthracite	7.2 lb/10^9 Btu	60	A
Lignite	1.2 lb/10^9 Btu	310	A
Industrial Boilers			
Bituminous	9.4 lb/10^9 Btu	14,400	A
Anthracite	7.2 lb/10^9 Btu	110	A
Lignite	1.2 lb/10^9 Btu	50	A

(continued)

TABLE 1-1. (CONTINUED)

Source	Emission factor[a]	Emissions (tons/yr)	Emission factor accuracy rating
Residential Boilers			
Bituminous	6.87 lb/10^9 Btu	150	C
Anthracite	4.95 lb/10^9 Btu	50	C
Lignite	6.34 lb/10^9 Btu	--	C
Hydrogen Fluoride Manufacture			
Tail gas vent			
uncontrolled	25.0 lb/ton	--	E
controlled - caustic scrubber	0.2 lb/ton	21.3	E
Primary Aluminum Production			
Anode baking furnace	0.52 lb/ton	--	A
Prebaked reduction cell	4.9 lb/ton	9,300	A
Prebaked fugitive emissions	1.2 lb/ton	--	A
Vertical soderberg stud cells	0.6 lb/ton	1,800	A
VSS - fugitive emissions	4.9 lb/ton	--	A
Horizontal soderberg stud cells	1.9 lb/ton	2,200	A
HSS - fugitive emissions	2.2 lb/ton	--	A
Phosphate Fertilizer Industry			
Phosphoric acid production			
Reactor	0.37 lb/ton[c]	--	C
Condenser	0.043 lb/ton[c]	--	C
Controlled emissions	0.010 lb/ton[c]	150	C
Gypsum ponds	0.42 lb/ton[c]	6,400	D
Triple Superphosphate Manufacture			
Reactor/dryer (granulor)	21.0 lb/ton[d]		A
Controlled (granulor)	0.24 lb/ton[d]	0.21	A
Diammonium Phosphate Manufacture			
Dryers and coolers	0.3 lb/ton[d]	--	A
Ammoniator/granulator	0.3 lb/ton[d]	--	A
Controlled emissions	0.08 lb/ton[d]	245	A

[a]Emission factors are based on the rate of production for the specific source category unless otherwise noted.

[b]The emission factor units are lbs HCl/ton material burned.

[c]The emission factor units are lbs HF/ton phosphate rock processed.

[d]The emission factor units are lbs HF/ton P_2O_5.

total, and primary aluminum production, comprising almost 15 percent, are the major hydrogen fluoride sources. Other sources include the fertilizer industry and the hydrogen fluoride manufacturing industry.

The rates at which HCl and HF are emitted during coal combustion are functions of coal composition and air pollution control techniques. A study of coal combustion in utility boilers conducted by the Bureau of Mines found the majority of chlorine contained in coal to volatilize and form HCl. There is a need for additional scientific data which directly assesses the chemical form of fluorine emitted during coal combustion. In lieu of such data and because of the chemical similarity between fluorine and chlorine, it is assumed that all fluorine in the feed coal reacts to form HF.

Data compiled in 1979 on trace element compositions in coal were obtained from studies by TRW and GCA and were used to calculate emission factors for coal combustion in utility and industrial boilers. Factors calculated for bituminous coal burned in utility boilers are 78.8 lbs HCl/10^9 Btu and 9.4 lbs HF/10^9 Btu. These factors were assigned an A ranking due to the number of tests conducted, availability of information concerning accuracy, and type of test methods used. Recent data (1985) developed by the Department of Energy's Pittsburgh Energy Technology Center from lab tests on bituminous coal in utility boilers resulted in emission rates of 690 lbs Cl per 10^9 Btu per percent Cl and 870 lbs per 10^9 Btu per percent F. Dividing by the chlorine and fluorine contents of the coal and assuming that emissions are in the form of HCl and HF result in emission factors of 28 lbs HCl/10^9 Btu and 4.7 lbs HF/10^9 Btu. These factors compare favorably with those developed from the TRW/GCA study.

Scrubbers, electrostatic precipitators (ESP's), cyclones, and baghouses are used frequently on coal-fired utility boilers as flue gas control techniques. The primary purpose of these controls is to remove particulate matter from the flue gas stream. The efficiency of wet scrubbing devices has been reported at about 80 percent for HCl and HF emissions from bituminous coal-fired utility boilers. Baghouses which have sorbent or alkaline materials introduced may remove a substantial amount of HCl and HF. A study of the use of nacholite and sodium bicarbonate as dry sorbent resulted in a 95

to 98 percent HCl removal. However, under normal operating practices, baghouses, ESP's, and cyclones have no significant effect on removal of HCl or HF.

Another control technique, flue gas desulfurization, is used to remove sulfur oxides from coal combustion. Data have indicated that flue gas desulfurization is at least 95 percent effective in removal of HCl. No data are available to quantify removal efficiencies of HF.

Several emission factors received low ratings because of limited data. Factors for HCl from residential boilers, hydrochloric acid manufacturing, and waste incineration received intermediate to poor rankings because of the small number of plants actually tested and the absence of information concerning test methodology. Factors for HF emissions from residential boilers, phosphoric acid production, and hydrogen fluoride manufacture were assigned low rankings based upon the low number of studies, absence of information concerning accuracy of test methods, and the number of assumptions made in determining these factors. Additional data which address emission rates of HCl and HF from these sources would be beneficial.

SECTION 2
INTRODUCTION

The National Acid Precipitation Assessment Program (NAPAP) was established by Congress in 1980 to coordinate and expand research on problems posed by acid deposition in and around the United States. The program is managed through ten task groups having specific technical responsibilities. One of these groups, Task Group B: Man-Made Sources, is charged with providing a complete and accurate nationwide inventory of emissions from man-made sources thought to be important in acid deposition processes.

The purpose of this report is to compile and assess emission factors available for hydrogen chloride (HCl) and hydrogen fluoride (HF) and to identify areas where better data are needed. When available, emission factors based on tests performed by a sound methodology and accompanied by adequate background data are presented. Emission factors were evaluated on a scale of A through E with an A representing data from a large data base covering a good cross section of the industry, determined from valid test methods, and with a high confidence level. Data rated E were developed from a small data base, not necessarily representative of the industry, and with a low confidence level. Ratings of B through D represent data with intermediate confidence levels.

Section 3 presents a discussion of coal combustion. Because coal combustion accounts for over 89 percent of the hydrogen chloride and 78 percent of the hydrogen fluoride, Section 3 discusses this source category separately and presents emission factors for both compounds from this source category. Section 4 presents emission factors for other major stationary sources of hydrogen chloride, including incineration, propylene oxide manufacture, and by-product hydrochloric acid production. Section 5 presents emission factors for other major stationary sources of hydrogen fluoride, including primary aluminum production, the fertilizer industry, and hydrogen fluoride manufacture.

The NAPAP emissions inventory is being prepared for base year 1980. Therefore, nationwide industry breakdown and emissions estimates given in the following sections generally are for that year. However, emission factors were developed using the most recent data available.

SECTION 3
COAL COMBUSTION

INTRODUCTION

Coal combustion is the single largest source of gaseous hydrogen chloride (HCl) and hydrogen fluoride (HF) emissions. Coal combustion is discussed separately because of the complexity of the parameters that affect emissions from coal combustion, and because coal combustion emits both pollutants.

Coal is burned for three major applications--industrial, utility, and residential energy. When coal is burned, HCl and HF are produced and emitted to the atmosphere as combustion products. The quantity of HCl and HF emitted to the atmosphere are functions of coal composition, method of combustion, and air pollution control techniques. This section describes each of the factors that influence these emissions and provides estimates of emission factors based on data currently available. Studies are being conducted by the Department of Energy to quantify HCl and HF emissions from coal combustion more accurately. Preliminary results from these studies are included in this report.

Chlorine and Fluorine in Coal Combustion Products

A breakdown of coal consumption by sector for 1980 is presented in Table 3-1. The majority of the research conducted on coal combustion has been on utility boilers, since utility boilers account for the majority of the coal consumed.

Based on a study of coal combustion in utility boilers conducted by the Bureau of Mines, the majority of chlorine contained in coal is believed to volatilize and form HCl.[2] Thermodynamic equilibrium calculations performed during the same study indicate that small amounts of other gaseous chlorine compounds, such as Cl_2, HOCl, and NOCl, can be formed during coal combustion; however, during laboratory simulation their presence was not detected. In the

TABLE 3-1. UNITED STATES COAL CONSUMPTION BY SECTOR, 1980[a]

Consuming sector	Percent of total coal consumption	Coal consumption (10^{15} Btu)
Commercial	0.6	0.095
Industrial	20.5	3.181
Residential	0.4	0.065
Electrical generation	78.5	12.151
Total	100.0	15.492

[a]Reference 1.

laboratory tests, the Bureau of Mines used an ice trap to capture all condensible species of chlorine escaping in the flue gas. The chlorine content of the bath was analyzed by the Volhard technique to determine total chloride ion and by acidimetric titration to determine the HCl content. The results of these two measurement techniques were identical, indicating that chlorine in the flue gas is in the form of HCl.

Tests performed by the Bureau of Mines found that only 1.6 to 7.1 percent of the incoming chlorine remained in the ash.[2] Another study conducted by the Oak Ridge National Laboratory found less than one percent of the chlorine in the boiler slag, outlet fly ash, or inlet fly ash.[3] The impinger solutions of the flue gas sampling trains were not analyzed for chlorine in this study. However, the study concluded that chlorine remains completely in a gaseous phase following combustion. During the Oak Ridge study, fluorine also was investigated; however, since the results were variable and nonreproducible, they were not reported.

There is a need for additional scientific data which directly assess the form fluorine takes during coal combustion. In lieu of such data, it is assumed that all fluorine in the feed coal volatilizes to form HF. This assumption is used later in this section in the development of emission factors.

Chlorine and Fluorine Content of Coals

Coal is formed over eons from successive layers of fallen vegetation. As vegetation accumulates, physical and chemical changes, such as loss of water and volatile matter, occur. Over time, the vegetation turns from peat to lignite, the earliest stage in the formation of coal. As lignite is compressed with deeper burial, the heat associated with the compression drives off additional volatile components. As more volatile components are driven off, the rank and quality of the coal increase from lignite to subbituminous, bituminous, and anthracite.[4] These various types of coal can be found throughout the continental United States as shown in Figure 3-1.[5]

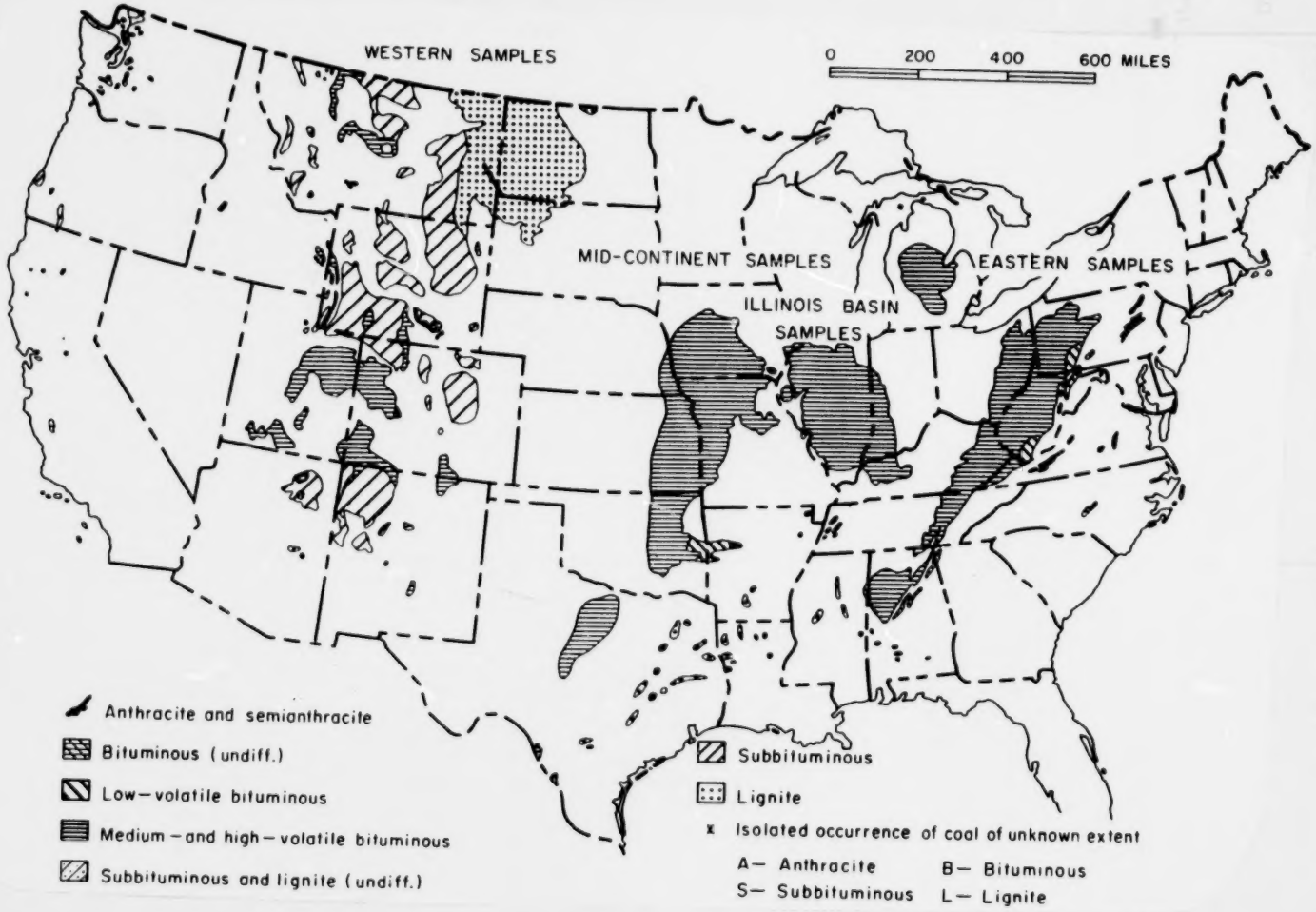

Figure 3-1. Coal fields of continental United States showing coal class and regional designations.[5]

A great deal of literature currently exists on the elemental chlorine and fluorine content of various coals. As shown in Tables 3-2 and 3-3, chlorine and fluorine concentrations of domestic coals vary over a large range. There is a great deal of variation within the same type of coal, as well. For example, in Table 3-2 there are four different values for bituminous coal, each of which is an average of a number of samples. In addition, chlorine and fluorine content of coal can vary dramatically within a particular seam. The coal fields with the highest chlorine content are in the Illinois basin as seen in Table 3-3. Generally the chlorine content of the Illinois coals increases with the depth of the seam. Coals mined by surface methods are low in chlorine (<0.04 percent), while coals mined at greater depths may have chlorine concentrations from 0.4 to 0.6 percent. Western coals have a relatively low chlorine content.[5]

The molecular form of chlorine and fluorine in coal is not understood clearly. Chlorine in coal exists in both organic and inorganic forms. A study was conducted by the Illinois State Geological Survey to determine the volatilities of trace and minor elements in coal during pyrolysis. Seven coals were studied: five from the Illinois basin; one North Dakota lignite; and one medium volatility coal from Alabama. Chlorine was analyzed by X-ray fluorescence and found to be volatile even at the low temperatures used in the study (840°F and 1110-1290°F). It was concluded that chlorine occurs in coal in a form more volatile than sodium chloride.[11] However, no correlation has been developed between the molecular form of chlorine or fluorine in coal and the molecular form of chlorine or fluorine in combustion products.

COAL COMBUSTION IN UTILITY BOILERS

There are three principal types of coal-fired utility boilers: stoker-fired, cyclone furnaces, and pulverized coal-fired (PC-fired). The characteristic difference between the boiler types is the feed mechanism. Of the three types currently used, PC-fired is the most common.

TABLE 3-2. CHLORINE AND FLUORINE CONTENTS OF VARIOUS COALS BY COAL TYPE

Type of Coal	Average Concentration of F and Cl			
	F (ppm) by weight	Number of samples	Cl (ppm) by weight	Number of samples
Anthracite[a]	61	53	--	--
Anthracite[b]	81.5	36	404	3
Subbituminous[a]	63	183	255	183
Bituminous[a]	77	509	--	--
Bituminous[b]	102	86	852	48
Eastern bituminous[b]	87	52	1,064	30
Western bituminous[b]	141	34	292	18
Lignite[a]	94	54	110	54
North Dakota lignite[b]	27.5	7	63.5	7
Texas lignite[b]	47	18	<290	24
All Coals[a]	74	799	207	--

[a]References 6 and 7.

[b]Reference 8.

TABLE 3-3. CHLORINE AND FLUORINE CONTENTS OF VARIOUS COALS BY STATE AND REGION

State or Region	Average Concentration of F and Cl			
	F (ppm) by weight	Number of samples	Cl (ppm) by weight	Number of samples
Alabama[a]			220	13
Alaska	90[b]	18[b]	70[a]	3[a]
Arizona[a]			100	2
Colorado[a]			70	94
Illinois[a]			1,900	44
Indiana[a]			400	12
Kentucky[a]			1,100	58
Montana[a]			20	10
New Mexico[a]			160	41
North Dakota[a]			90	45
Ohio[a]			910	58
Pennsylvania[a]			1,300	174
South Dakota[a]			100	5
Tennessee[a]			850	12
Utah[a]			80	94
Virginia[a]			670	17
Washington[a]			0	4
West Virginia[a]			1,080	231
Wyoming[a]			100	18
Appalachian Region[b]	80	331		
Interior Province[b]	71	143		
Gulf Province[b]	124	34		
Northern Great Plains Province[b]	45	93		
Rocky Mountain Province[b]	70	124		
Southern Appalachian[c]			1,300	22
Northern Appalachian[c]			1,000	130
Eastern Mid-west[c]			800	2
Western Mid-west[c]			900	22
Western Region[c]			300	40
Total U.S.[c]			900	220

[a]Reference 9.
[b]Reference 7.
[c]Reference 10.

Stoker-fired Boilers

Stoker-fired boilers were developed early in the history of the steam boiler, replacing hand firing. In this design, coal is fed onto a grate within the furnace. There are many types of stokers available; however, due to their inefficiency, their use in large power plants is diminishing. They are still used in industrial applications and in smaller power plants.

Cyclone Furnaces

Cyclone furnaces are used in existing power plants. Construction of new utility-sized cyclone furnaces, however, has been reduced due to excessive nitrogen oxide emissions. With certain types of coals, cyclone furnaces show reductions in the flue gas fly ash concentration, savings in coal preparation costs, and reductions in furnace size relative to pulverized-coal-fired furnaces. Prior to combustion in a cyclone furnace, coal is crushed in a simple crusher so that approximately 95 percent will pass through a 4-mesh screen. Approximately 20 percent of the required combustion air, termed primary air, is introduced tangentially to the burner, imparting a whirling motion to the incoming coal. Secondary air also is introduced tangentially and imparts a further whirling or centrifugal action to the coal particles. Cyclones are capable of burning a large variety of coal types. Coals with high sulfur content, a high iron-to-magnesium ratio, or a high iron-to-calcium ratio, however, are not considered suitable.[12]

Pulverized Coal Boilers (PC boilers)

The most widely used boiler type is the pulverized-coal-fired boiler. Coal is pulverized in a mill until 70 percent of the particles will pass through a 200 mesh sieve. The pulverized coal then is suspended in air and fed through burners into a combustion chamber. Approximately 15 to 20 percent of the air required for combustion is used to transport the pulverized coal.

Secondary air is introduced at the burner and comprises the remainder of the combustion air. PC boilers typically operate at 15 percent excess air.[12] The PC boiler can be a wet or dry bottom type depending on the method of ash removal. The majority of the ash removed from a dry bottom furnace is in the form of dust with approximately 80 percent of the ash originally in the coal leaving the furnace entrained in the flue gas. In a wet-bottom or slag-tap PC boiler, approximately one-half the ash leaving the furnace is dust and the other half is molten slag. The molten slag is drained from the bottom of the furnace. Typically, dry bottom furnaces fire coals with high ash fusion temperatures. Pulverized dry bottom boilers burning bituminous coal represent approximately 73 percent of the industry. Pulverized wet bottom boilers are being phased out due to their inability to meet nitrogen oxide air pollution standards.[8]

Air Pollution Control Techniques

Scrubbers, electrostatic precipitators (ESP), cyclones, and baghouses are used frequently as flue gas control techniques. These control devices are effective for different pollutants and often are used in combination. This subsection describes the operation of these control devices and their effect on HCl and HF emissions. Table 3-4 shows the distribution of particulate control equipment for utility boilers burning bituminous coal.[13]

An ESP imparts an electrical charge onto particles in the flue gas. An opposite charge is placed on the collecting medium, either metal plates or wires, and the charged particles are pulled out of the flue gas. The dust is collected by rapping the collection medium. Until the latter half of the 1970's the preferred method for particulate control was ESP's.[13] An ESP can achieve a particulate control efficiency of 99.9 weight percent. An ESP, however, has no demonstrated effect on HCl or HF emissions.

TABLE 3-4. DISTRIBUTION OF PARTICULATE CONTROL EQUIPMENT FOR UTILITY BOILERS BURNING BITUMINOUS COAL[a]

Combustion system category	Percent distribution of particulate control equipment			
	ESP	Centrifugal separator	Other[b]	No control
Pulverized dry bottom				
Number basis	60	17	15	8
Capacity basis	79	10	10	2
Fuel consumption basis	83	11	5	1
Pulverized wet bottom				
Number basis	52	21	16	11
Capacity basis	66	11	9	14
Fuel consumption basis	77	9	7	7
Cyclone				
Number basis	70	5	18	7
Capacity basis	83	8	5	4
Fuel consumption basis	89	5	3	3
Stoker				
Number basis	8	35	25	32
Capacity basis	29	32	20	19
Fuel consumption basis	45	25	14	16

[a]Reference 13.

[b]Wet scrubbers, fabric filters, gravitational separators.

Baghouses or fabric filters usually are designed as a series of dacron bags through which the flue gas passes before exiting through the stack. Particles entrained in the flue gas are caught in the fabric. The bags are cleaned either by shaking or by applying a negative pulse of air. Baghouses can achieve high particle control efficiencies. They generally do not affect the removal efficiency of HCl or HF unless a sorbent is introduced to chemically bond to the particles. Alkaline materials sometimes are used to aid in the removal of sulfur compounds. This also will result in a removal of HCl or HF.

Baghouse use as a control device for both industrial and utility boilers is increasing. A study conducted by the Department of Energy showed that fabric filtration in combination with the injection of a dry sorbent can be very effective in controlling HCl emissions resulting from the combustion of bituminous coal in a 500 lb/hr furnace.[14] This study used nacholite and sodium bicarbonate as the dry sorbent and effected approximately 95 to 98 percent HCl removal.

Cyclones or centrifugal separators also are used in the control of particles from utility boilers. A multiple cyclone separator consists of a number of small-diameter cyclones operating in parallel with a common gas inlet and outlet. The principle of operation is centrifugal separation of suspended particles from the gas stream. Major design criteria affecting the efficiency of a cyclone are gas velocity, and diameter and length of the cyclone cylinder. Cyclones can handle a wide range of chemical and physical conditions in the inlet gas stream. They often are used before other high efficiency control devices in order to reduce the ash collection burden on the high efficiency device.[15] Cyclones are assumed to have no effect on HCl or HF emissions.

Wet scrubbers also are used to remove particles from flue gas streams. A wet scrubber can use a variety of methods to wet the contaminant particles in order to remove them from the gas stream. The simplest type of scrubber is a chamber in which spray nozzles are placed. The gas stream velocity decreases as it enters the chamber, and the wetted particles settle and are collected at the bottom of the chamber. A cyclone-type scrubber introduces a liquid spray

into the rotating gas. The atomized fine-spray droplets are captured in the rotating gas stream and are swept across to the walls of the cylinder, colliding with, absorbing, and collecting the dust or fume particles. Orifice-type scrubbers direct the flow of air through a restricted passage partially filled with water. The dispersed water through centrifugal forces, impingment, and turbulence causes wetting of the particles and their collection. Most wet scrubbers recycle the wetting medium, which typically is water. The efficiency of a wet scrubbing device for HCl or HF emissions control should be greater than that of a baghouse or ESP. One reference[8] reports control efficiencies for wet scrubbers to be about 80 percent for HCl and HF emissions from bituminous coal-fired utility boilers.

Methods for control of gaseous air pollutants generally differ from those used for particulate control. Gas absorption is used to control sulfur dioxide, hydrogen sulfide, HCl, chlorine, HF, oxides of nitrogen, and light hydrocarbons. Gas absorption equipment is designed to provide thorough contact between the gas and liquid solvent in order to permit interphase diffusion of the materials. No data on HCl or HF removal are available.

Gaseous sulfur compounds typically are removed from flue gas streams by flue gas desulfurization (FGD) systems. Flue gases can be treated through wet, semidry or dry desulfurization of either the throwaway type, in which all waste stream are discarded, or the recovery (regenerable) type, in which the SO_x absorbent is regenerated and reused. To date, wet systems are the most commonly applied.[16] Removal of HCl from flue gases with FGD systems is very high.[17] In tests conducted with dry FGD systems utilizing nacholite and sodium bicarbonate as sorbents, a 95 percent removal was obtained.[14] Little data are available to quantify HF removal efficiency of FGD systems.

In gas adsorption, molecules from a gas stream contact and adhere to the surface of a solid. Commonly used adsorbents are activated carbon, alumina, and bauxite. Adsorption can occur until the saturation level of the adsorbent is reached (breakthrough). After breakthrough the adsorbent material must be either regenerated or replaced. Gas adsorption can be effective in removing gaseous air pollutants such as sulfur dioxide, HCl, HF, chlorine gas, and nitrogen oxide.[15] The actual removal efficiencies for HCl and HF have not been quantified accurately.

Emission Factors for Utility Boilers

The most prevalent type of coal burned in the utility sector is bituminous. In 1978, 350 million tons of eastern bituminous and anthracite coal, 130 million tons of western bituminous coal, and 34 million tons of lignite were consumed by the utilities. Major increases in the consumption of western bituminous and lignite are projected primarily because these coals have a lower sulfur content.[8]

Emission factors for utility boilers were developed by TRW, Inc. in an EPA-funded study.[8] The emission factors were developed using enrichment factors. Trace elements found in coal were divided into the following three classes: (1) those which divide equally in the fly ash and the bottom ash (class I); (2) those which are enriched in the fly ash relative to the bottom ash (class II); and (3) those which are discharged to the environment as gases (class III). Chlorine and fluorine species were assumed to be in class III. Studies on trace-element vaporization by Quann, et al. also indicate that chlorine species would be in class III.[18] Particulate control devices such as mechanical collection and electrostatic precipitators were assumed to remove 80 percent of the halogens; however, wet scrubbers are used to control only a small amount of coal combustion (less than 5 percent of coals burned in utility and industrial boilers and none of the coals burned in residential boilers are controlled by wet scrubbers).

Emission factors were developed based on average properties of coal being consumed, boiler type, and associated air pollution control devices. A pulverized dry bottom boiler equipped with an ESP and burning bituminous coal is the most common furnace configuration found in the utility industry today.[8]

Recently, new emission factors for Cl and F have been developed by the Department of Energy's Pittsburgh Energy Technology Center (PETC) from laboratory tests on coal-fired utility boilers. Preliminary results from these tests have been reported.[19] The tests utilized Kentucky bituminous coal with chlorine concentrations ranging from 356 ppm ($\pm$200) to 635 ppm and fluorine concentrations ranging from 51 ppm ($\pm$32) to 74 ppm. The test results indicated emission rates of 690 lbs Cl per 10^9 Btu per percent Cl and 870 lbs

F per 10^9 Btu per percent F. Dividing by the chlorine and fluorine contents of the coal and assuming that emissions are in the form of HCl and HF results in emission factors of 28 (±17) lbs HCl/10^9 Btu and 4.7 (±2.9) lbs HF/10^9 Btu.[19]

COAL COMBUSTION IN INDUSTRIAL BOILERS

Industrial boilers are smaller than utility boilers and are used by industry to provide steam or hot water. Only 10 to 15 percent of the industrial boilers are classified by heat transfer method, arrangement of heat transfer surface, and fuel feed system. The three types of heat transfer systems are watertube, firetube, and cast iron. Most newly installed industrial boilers are either watertube or firetube. Fuel feed systems are the same as discussed under utility boilers--stoker, cyclone, and PC-fired.

Watertube boilers

Watertube boilers are used in a variety of applications, ranging from supplying large amounts of process steam to providing space heat for industrial facilities. Watertube boilers are designed to pass water through the inside of heat transfer tubes while the outside of the tubes is heated by direct contact with hot combustion gases. This process results in generation of high-pressure, high-temperature steam.[20]

Firetube boilers

Firetube boilers are used primarily for industrial process steam production and in heating systems. In packaged firetube boilers, the hot gas flows through the tubes, and the water being heated circulates outside the tubes.[20]

Cast iron boilers

In cast iron boilers, the hot gas is contained inside the tubes and the water being heated circulates outside the tubes. Cast iron boilers are used to produce either low-pressure steam or hot water.[20] Cast iron boilers operate at generally less than 2.9 MW (10×10^6 Btu/hr) thermal input.

Emission Factors for Industrial Boilers

Emission factors for HCl and HF have not been developed for industrial boilers. Emission factors developed for utility boilers can be used for industrial boilers when the type of boiler and fuel are the same.[13] Air pollution control technologies for industrial boilers are the same as those discussed under utility boilers. Industrial boilers use ESP's, fabric filters, and multiple cyclones for particulate control.[21] Table 3-5 presents a 1978 breakdown of particulate control systems used by industrial boilers. Flue gas desulfurization control techniques for industrial boilers are the same as those used for utility boilers. These techniques typically rely on a calcium- or sodium-based sorbent to react with the sulfur dioxide to form a sulfide or sulfate salt, which is then removed from the flue gas stream.

COAL COMBUSTION IN RESIDENTIAL BOILERS

At the present time, approximately 1 percent of the nation's homes are heated with coal. Estimated 1980 residential consumption of coal for primary heating was 6.50×10^{12} Btu (2,610,000 tons), consisting of 21.8×10^{12} Btu (853,000 tons) of anthracite and 43.2×10^{12} Btu (1,760,000 tons) of butuminous and lignite. Coal was burned in approximately 490,000 heating devices located in all 50 states. Lignite is burned for residential heating in North Dakota only; anthracite combustion is limited to northern states east of the Mississippi River with 64 percent in Pennsylvania; and bituminous coal is burned in every state except Connecticut, Delaware, Maine, Maryland, New Hampshire, New Jersey, North Dakota, Rhode Island, and Vermont. About 70 percent of all residential coal heating devices are located in the Appalachian coal region including the States of Alabama, Kentucky, Maryland,

TABLE 3-5. CONTROL SYSTEMS USED FOR INDUSTRIAL BOILERS[a]

Control technique	Percent (by number)
No control	33
Cyclone	48
Scrubber	4
Electrostatic precipitator	14
Fabric filter	1

[a]Reference 13.

Ohio, Pennsylvania, Tennessee, Virginia, and West Virginia. Pennsylvania alone has 28 percent of all coal-fired heating units and accounts for 30 percent of total residential coal consumption. In 1970, approximately 55 percent of the coal-fired residential primary heating devices were boilers and warm-air furnaces; the remaining units were heating stoves.[6]

In a study conducted by Monsanto Research Corporation for EPA, uncontrolled emission factors from residential combustion of coal were compiled. These emission factors are subdivided by coal type with 60.5×10^{-9} lbs HCl/Btu of fuel and 6.86×10^{-9} lbs HF/Btu of fuel from bituminous, 120.0×10^{-9} lbs HCl/Btu of fuel and 4.95×10^{-9} lbs HF/Btu of fuel from lignite combustion. In this study all of the chlorine and fluorine present in coal was assumed to be emitted to the atmosphere.

SUMMARY

Tables 3-6 and 3-7 present a summary of emission factors and total nationwide emissions of HCl and HF, respectively. Source classification codes and emission factors for HCl and HF are summarized separately in Table 3-8.

TABLE 3-6. SUMMARY OF EMISSIONS AND EMISSION FACTORS FOR HCl FROM UTILITY, INDUSTRIAL, AND RESIDENTIAL COAL BOILERS

	Emission factor[a] (lbs HCl/10^9 Btu)	Coal consumption (10^{15} Btu/yr)	Emission rate (10^3 tons HCl/yr)
Utility boilers[b]			
Bituminous (SCC 1-01-002)			
PC fired	78.8	10.23	403.1
Stokers	78.8	0.10	3.9
Cyclones	78.8	1.30	51.2
Anthracite (SCC 1-01-001)			
PC fired	35.5	0.006	0.11
Stokers	35.5	0.011	0.20
Lignite (SCC 1-01-003)			
PC fired	1.0	0.41	0.21
Stokers	1.0	0.01	0.01
Cyclones	1.0	0.09	0.05
Total		12.15	458.8
Industrial boilers[c]			
Bituminous (SCC 1-02-002)			
PC fired	78.8	1.81	71.3
Stokers	78.8	1.18	46.5
Cyclones	78.8	0.08	3.2
Anthracite (SCC 1-02-001)			
Stokers	35.5	0.03	0.53

(continued)

TABLE 3-6. (CONTINUED)

	Emission factor[a] (lbs HCl/10^9 Btu)	Coal consumption (10^{15} Btu/yr)	Emission rate (10^3 tons HCl/yr)
Industrial boilers[c] (cont'd)			
Lignite (SCC 1-02-003) Stokers	1.0	0.08	0.04
Total		3.18	121.6
Residential boilers[d]			
Bituminous (SCC 1-03-002)	60.5	0.043	1.3
Anthracite (SCC 1-03-001)	120	0.022	1.3
Lignite (SCC 1-03-003)	35.1	--	--
Total		0.065	2.6
TOTAL		15.4	583.0

[a]Emission factors were converted assuming that all of the chlorine was emitted as hydrogen chloride. While wet scrubbers and FGD systems are the only controls used on boilers that have a significant effect on HCl removal, they are used to control only a small percentage of coal burned in utility and industrial boilers and are not used on residential boilers. Therefore, uncontrolled and controlled emission factors for HCl are considered to be the same.

[b]Coal consumption estimates for 1980 were calculated by multiplying the total coal consumption by the percent coal burned in each type of boiler. See references 1 and 8.

[c]Coal consumption estimates for 1980 were calculated by multiplying the total coal consumption by the percent coal burned in each type of boiler. See references 1 and 13.

[d]Based on 1980 data. See reference 1. Average heating values for the three coal types are: Bituminous 12,260 Btu/lb; Anthracite 12,780 Btu/lb; Lignite 5,000 Btu/lb.

TABLE 3-7. SUMMARY OF EMISSIONS AND EMISSION FACTORS FOR HF FROM UTILITY, INDUSTRIAL, AND RESIDENTIAL COAL BOILERS

	Emission factor[a] (lbs HF/10^9 Btu)	Coal consumption (10^{15} Btu/yr)	Emission rate (10^3 tons HF/yr)
Utility boilers[b]			
Bituminous (SCC 1-01-002)			
PC fired	9.4	10.23	48.1
Stokers	9.4	0.10	0.47
Cyclones	9.4	1.30	6.1
Anthracite (SCC 1-01-001)			
PC fired	7.2	0.006	0.02
Stokers	7.2	0.011	0.04
Lignite (SCC 1-01-003)			
PC fired	1.2	0.41	0.25
Stokers	1.2	0.01	0.01
Cyclones	1.2	0.09	0.05
Total		12.15	55.0
Industrial boilers[c]			
Bituminous (SCC 1-02-002)			
PC fired	9.4	1.81	8.5
Stokers	9.4	1.18	5.5
Cyclones	9.4	0.08	0.38
Anthracite (SCC 1-02-001)			
Stokers	7.5	0.03	0.11

(continued)

TABLE 3-7. (CONTINUED)

	Emission factor[a] (lbs HF/10^9 Btu)	Coal consumption (10^{15} Btu/yr)	Emission rate (10^3 tons HF/yr)
Industrial boilers[c] (cont'd)			
Lignite (SCC 1-02-003) Stokers	1.2	0.08	0.04
Total		3.18	14.5
Residential boilers[d]			
Bituminous (SCC 1-03-002)	6.87	0.043	0.15
Anthracite (SCC 1-03-001)	4.95	0.022	0.05
Lignite (SCC 1-03-003)	6.34	--	--
Total		0.065	0.20
TOTAL		15.4	69.5

[a]Emission factors were converted assuming that all of the fluorine emitted was hydrogen fluoride. While wet scrubbers and FGD systems are the only controls used on boilers that have a significant effect on HF removal, they are used to control only a small percentage of coal burned in utility and industrial boilers and are not used on residential boilers. Therefore, uncontrolled and controlled emission factors for HF are considered to be the same.

[b]Coal consumption estimates for 1980 were calculated by multiplying the total coal consumption by the percent coal burned in each type of boiler. See references 1 and 8.

[c]Coal consumption estimates for 1980 were calculated by multiplying the total coal consumption by the percent coal burned in each type of boiler. See references 1 and 13.

[d]Based on 1980 data. See reference 1. Average heating values for the three coal types are: Bituminous 12,260 Btu/lb; Anthracite 12,780 Btu/lb; Lignite 5,000 Btu/lb.

TABLE 3-8. COAL COMBUSTION SCCs

Source	SCC	Emission factor[a]	
		HF	HCl
External combustion boilers - electric generation			
Anthracite coal			
pulverized coal	1-01-001-01	0.18	0.91
traveling grate stokers	1-01-001-02	0.18	0.91
Bituminous coal			
pulverized coal: wet bottom	1-01-002-01	0.23	1.9
pulverized coal: dry bottom	1-01-002-02	0.23	1.9
cyclone	1-01-002-03	0.23	1.9
spreader stoker	1-01-002-04	0.23	1.9
traveling grate (overfeed) stoker	1-01-002-05	0.23	1.9
pulverized coal: dry bottom (tangential firing)	1-01-002-12	0.23	1.9
atmospheric fluidized bed	1-01-002-17	0.23	1.9
Subbituminous coal			
pulverized coal: wet bottom	1-01-002-21	0.23	1.9
pulverized coal: dry bottom	1-01-002-22	0.23	1.9
cyclone	1-01-002-23	0.23	1.9
spreader stoker	1-01-002-24	0.23	1.9
traveling grate (overfeed) stoker	1-01-002-25	0.23	1.9
pulverized coal: dry bottom (tangential firing)	1-01-002-26	0.23	1.9
Lignite			
pulverized coal	1-01-003-01	0.01	0.01
pulverized coal: tangential firing	1-01-003-02	0.01	0.01
cyclone	1-01-003-03	0.01	0.01
traveling grate (overfeed) stoker	1-01-003-04	0.01	0.01
spreader stoker	1-01-003-06	0.01	0.01
External combustion boilers - industrial			
Anthracite coal			
pulverized coal	1-02-001-01	0.18	0.91
traveling grate stokers	1-02-001-04	0.18	0.91
hand-fired	1-02-001-07	0.18	0.91
Bituminous coal			
pulverized coal: wet bottom	1-02-002-01	0.23	1.9
pulverized coal: dry bottom	1-02-002-02	0.23	1.9
cyclone	1-02-002-03	0.23	1.9
spreader stoker	1-02-002-04	0.23	1.9
overfeed stoker	1-02-002-05	0.23	1.9
underfeed stoker	1-02-002-06	0.23	1.9

CONTINUED

TABLE 3-8. (CONTINUED)

Source	SCC	Emission factor[a]	
		HF	HCl
pulverized coal: dry bottom (tangential firing)	1-02-002-12	0.23	1.9
atmospheric fluidized bed	1-02-002-17	0.23	1.9
Subbituminous coal			
pulverized coal: wet bottom	1-02-002-21	0.23	1.9
pulverized coal: dry bottom	1-02-002-22	0.23	1.9
cyclone	1-02-002-23	0.23	1.9
spreader stoker	1-02-002-24	0.23	1.9
traveling grate (overfeed) stoker	1-02-002-25	0.23	1.9
pulverized coal: dry bottom (tangential firing)	1-02-002-26	0.81	1.9
Lignite			
pulverized coal	1-02-003-01	0.01	0.01
pulverized coal: tangential firing	1-02-003-02	0.01	0.01
cyclone	1-02-003-03	0.01	0.01
traveling grate (overfeed) stoker	1-02-003-04	0.01	0.01
spreader stoker	1-02-003-06	0.01	0.01
External boilers - commercial/institutional			
Anthracite coal			
pulverized coal	1-03-001-01	0.13	3.07
traveling grate stokers	1-03-001-02	0.13	3.07
hand-fired	1-03-001-03	0.13	3.07
Bituminous coal			
pulverized coal: wet bottom	1-03-002-05	0.17	1.48
pulverized coal: dry bottom	1-03-002-06	0.17	1.48
overfeed stoker	1-03-002-07	0.17	1.48
underfeed stoker	1-03-002-08	0.17	1.48
spreader stoker	1-03-002-09	0.17	1.48
hand-fired	1-03-002-14	0.17	1.48
pulverized coal: dry bottom (tangential firing)	1-03-002-16	0.17	1.48
atmospheric fluidized bed	1-03-002-17	0.17	1.48
Subbituminous coal			
pulverized coal: wet bottom	1-03-002-21	0.17	1.48
pulverized coal: dry bottom	1-03-002-22	0.17	1.48
cyclone	1-03-002-23	0.17	1.48
spreader stoker	1-03-002-24	0.17	1.48
traveling grate (overfeed) stoker	1-03-002-25	0.17	1.48
pulverized coal: dry bottom (tangential firing)	1-03-002-26	0.17	1.48

CONTINUED

TABLE 3-8. (CONTINUED)

Source	SCC	Emission factor[a]	
		HF	HCl
Lignite			
pulverized coal	1-03-003-05	0.063	0.351
pulverized coal: tangential firing	1-03-003-06	0.063	0.351
traveling grate (overfeed) stoker	1-03-003-07	0.063	0.351
spreader stoker	1-03-003-09	0.063	0.351

[a]References 6, 8, and 13. Emission factor units are lb/ton coal burned.

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SECTION 4
HYDROGEN CHLORIDE EMISSIONS

INTRODUCTION

This section presents hydrogen chloride (HCl) emission factors and total annual HCl emissions for various source categories. Coal combustion is the largest source of HCl emissions, accounting for 583,000 tons in 1980, and is discussed in detail in Section 3. HCl sources discussed in this chapter include waste incineration, propylene oxide production, and hydrogen chloride manufacture. Table 4-1 shows the major HCl emission sources and provides a summary of total emissions.

The rainwater acidity content in the northeastern United States was calculated by Cogbill and Likens to be 62 percent sulfuric acid, 32 percent nitric acid, and 6 percent HCl.[1] Although the acidity contribution of HCl is lower than those of sulfuric and nitric acids, it is still significant. HCl sources and mechanisms of formation and atmospheric reaction have not been identified completely.

Natural sources of chloride include salt spray from the oceans,[2,3] volcanic gases,[4] and upper atmospheric reactions.[5] The occurence of chlorine gas in air is rare because of its high reactivity; therefore, chloride compounds are more likely to be found.[4,6] Concentrations of chlorides in coastal and noncoastal areas range from 10 ppmv to 27,000 ppmv. Salt spray emissions estimated on a global scale are 545 to 1,360 x 10^6 tons per year.[7,8,9] Nordlie measured volcanic activity and found that chlorides are released in the magmatic gases.[10] Bartel estimated the global volcanic contribution of chloride to be 6.9 x 10^6 tons per year.[11]

TABLE 4-1. SOURCES OF HYDROGEN CHLORIDE EMISSIONS

Source	Emission factor (lbs/SCC Unit)	Reference No.	Emissions (tons/year)	SCC	SCC Units
Propylene Oxide Manufacture[a]	7.46	12	2,140	3-01-205-01	tons produced
Incineration[b]			75,000		
Municiple Refuse		17		5-01-001-01	tons burned
Multiple chamber	5.0			5-01-001-02	tons burned
Single chamber	5.0			5-01-005-07	tons burned
Conical design - Refuse	5.0				
Industrial wastes		18			
Multiple chamber	5.35			5-03-001-01	tons burned
Single chambe:	5.35			5-03-001-02	tons burned
Controlled air	5.35			5-03-001-03	tons burned
Conical design - Refuse	5.35			5-03-001-04	tons burned
Liquid Wastes	1.19	19		NA	tons burned
By-product Hydrochloric Acid Production		21			
(with final scrubber)	0.2				
(without final scrubber)	3.0			3-01-011-01	tons final acid
Coal Combustion[c]			583,000		

[a]Based on 1980 data.

[b]Based on 1970 data.

[c]Coal combustion as a source of HCl emissions is discussed in detail in Section 3.

PROPYLENE OXIDE MANUFACTURE

Propylene oxide is manufactured by chlorohydrination of propylene and peroxidation of propylene. HCl is emitted during the manufacture of propylene oxide by the chlorohydrination process. In the United States, approximately 65 percent of production is by chlorohydrination.[12]

In the chlorohydrination process, propylene, chlorine, and water react to form hypochlorous acid, HCl, and propylene chlorohydrin. Propylene is converted to propylene chlorohydrin at such a rate that the liquid effluent leaving the reactor contains only 3 to 4 percent propylene chlorohydrin.[13]

The dilute propylene chlorohydrin reactor effluent then is mixed with a 10 percent slurry of slaked lime and pumped to a hydrolyzer. Here the chlorohydrin is converted to propylene oxide. The overhead from the hydrolyzer, predominantly propylene oxide and water, is contaminated with propylene dichloride, chloropropenes from dehydrohalogenation of propylene chloride, and aldehyde from isomerization of propylene oxide. The oxide is purified by fractionation in multiple distillation columns to produce a specification grade product.[13]

From the reaction and purification steps, HCl is emitted during venting of inert gases. The emission factor for these sources is reported as 7.46 lbs HCl per ton of propylene oxide produced. This factor is derived from field sampling data.[14] Applying the emission factor to the level of propylene oxide production by the chlorohydrination process for 1980 (574×10^3 tons), emissions of 2,140 tons HCl are estimated for this source.[15]

INCINERATION

HCl is emitted during the incineration of wastes containing chlorinated hydrocarbons, chlorine-containing plastics such as polyvinyl chloride, and chlorine or chlorides, often in the form of common salt (sodium chloride). Incineration is a combustion process used to change the chemical or physical characteristics of waste by oxidation. Incineration produces inorganic solid residues (ash) and the exhaust gases, carbon dioxide and water vapor.[16]

HCl is emitted from three types of incinerators: (1) municipal incinerators that burn public garbage; (2) municipally-owned incinerators that burn primarily industrial wastes; and (3) incinerators that burn liquid wastes such as polychlorinated waste, waste oil, and various other hydrocarbon liquids. The public incineration of approximately 30 x 10^6 tons of collected refuse in the United States in 1970 produced estimated emissions of 75,000 tons of HCl.[17] The emission factor for this source is calculated as 5 lbs HCl/ton of refuse burned. Multipying the emission factor by the estimated amount of refuse incinerated in 1980, 58 x 10^6 tons, results in emissions of 145,000 tons HCl. This number may actually be higher due to an increase in the percentage of plastic components in refuse.

Emission factors for municipally-owned industrial waste incinerators range from 2.0 to 7.0 lbs HCl/ton of wastes burned with a mean value of 5.35 lbs/ton.[18] Source test information from which these factors were derived was acquired from reports for three uncontrolled incinerators.

Several sources were tested for emissions from incineration of liquid wastes. Emission factors from the test data ranged from 0.72 to 1.61 lbs HCl/ton of waste burned with a mean uncontrolled emission factor of 1.19 lbs/ton.[19]

Data on the level of material incinerated in the United States in municipally owned industrial incinerators and liquid waste incinerators are not available. Therefore, HCl emissions from these sources cannot be estimated.

HYDROGEN CHLORIDE MANUFACTURE

In 1972, 80 percent of the HCl produced in the United States was manufactured as a byproduct of the chlorination of organic compounds. Byproduct HCl is produced in the manufacture of chlorinated benzenes, chlorinated toluenes, vinyl chloride, fluorocarbons, carbon tetrachloride, toluene diisocyanate, glycerin, linear alkylsulfonate detergents, chloroform, methylene chloride, methyl chloride, trichloroethylene, perchloroethylene, chloral, hexachlorocyclopentadiene, chlorinated paraffins, ethyl chloride, and

other substances. Thus, HCl is a byproduct in any manufacturing process in which chlorine is used to substitute a chlorine atom for hydrogen in a chemical compound. HCl also is produced as a byproduct when a saturated chlorinated compound is dehydrochlorinated to produce an unsaturated compound that contains one less chlorine atom.[20]

The recovery of hydrogen chloride from the chlorination of an organic compound is the major source of hydrogen chloride emissions. The exit gas from the absorption or scrubbing system is the actual source of the hydrogen chloride emitted. By-product hydrogen chloride emission factors are 3 lbs/ton HCl produced without the final scrubber and 0.2 lbs/ton HCl produced with the final scrubber.[21] Multiplying the 1980 production of by-product HCl, 2,591,000 tons[22], by the uncontrolled emission factor gives a worst case emission estimate of 3,900 tons HCl.

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SECTION 5
HYDROGEN FLUORIDE EMISSIONS

INTRODUCTION

This section presents emission factors and total annual emissions for significant stationary sources of hydrogen fluoride (HF). Table 5-1 lists the major HF emission sources and provides a summary of total emissions, emission factors, and applicable SCC's. Coal combustion is the largest source of HF emissions, accounting for 69,500 tons in 1980, and is discussed in detail in Section 3.

Based on quantity of production, HF is the most important manufactured compound of fluorine; it is used directly or as an intermediate in the preparation of almost all fluorine-containing products.[1] The following sections describe the sources of atmospheric emissions of HF and report the HF emission factors. When necessary, data gaps are noted.

HYDROGEN FLUORIDE MANUFACTURE

HF is produced commercially by the reaction of fluorspar with sulfuric acid as shown in the following reaction:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Fluorspar typically contains 97.5 percent or more calcium fluoride, 1 percent or less silicon dioxide, and 0.05 percent or less sulfur.

TABLE 5-1. SOURCES OF HYDROGEN FLUORIDE EMISSIONS

Source	Emission Factor (lbs/SCC unit)	Reference No.	Emissions (tons/year)	SCC	SCC Units
Hydrogen Fluoride Manufacture[a]		2			
Rotary kiln (acid reactor)	0			3-01-012-02	tons acid produced
Tail gas vent					
uncontrolled	25.0				
controlled - caustic scrubber	0.2		21.3	3-01-012-06	tons acid produced
Primary Aluminum Production[b]		4			
Anode baking furnace	0.52				
Prebaked reduction cell	4.9			3-03-001-05	tons of molten aluminum produced
Prebaked fugitive emissions	1.2		9,300	3-03-001-01	tons of molten aluminum produced
Vertical soderberg stud cells	0.6			3-03-001-08	tons of molten aluminum produced
VSS - fugitive emissions	4.9		1,800	3-03-001-03	tons of molten aluminum produced
Horizontal soderberg stud cells	1.9			3-03-001-10	tons of molten aluminum produced
HSS - fugitive emissions	2.2		2,200	3-03-001-02	tons of molten aluminum produced
				3-03-001-09	tons of molten aluminum produced
Phosphate Fertilizer Industry[a]					
Phosphoric acid production[c]					
Reactor	0.37	6		3-01-016-01	tons phosphate rock processed
Condenser	0.043	6		3-01-016-03	tons phosphate rock processed
Controlled emissions	0.010	6	150	NA	tons phosphate rock processed
Gypsum ponds	0.42	9	6,400	3-01-016-02	tons phosphate rock processed
Triple Superphosphate Manufacture					
Reactor/drver (granulor)[d]	21.0	10			
Controlled (granulor)[d]	0.24	11		3-01-029-06	tons P_2O_5 produced
Cone/curing belt/conveyor (run of pile)[e]	0		0.21	NA	tons P_2O_5 produced
				3-01-029-05	tons P_2O_5 produced
Diammonium Phosphate Manufacture[d,f]					
Dryers and coolers	0.3	12			
Ammoniator/granulator	0.3	12		3-01-030-01	tons P_2O_5 produced
Controlled emissions	0.08	13		3-01-030-02	tons P_2O_5 produced
			245	NA	tons P_2O_5 produced
Coal Combustion[g]			69,500		

[a] Based on 1980 data.

[b] Based on 1980 data. Emission factors are weighted averages based on uncontrolled and controlled data. For uncontrolled and controlled factors refer to Table 5-2.

[c] The emission factor units are lb HF/ton phosphate rock processed. The numbers were calculated based on 0.333 ton P_2O_5/ton phosphate rock.

[d] Fluoride emissions from the triple superphosphate granulator process and the diammonium phosphate manufacturing process are reported as pounds of fluoride and are assumed to be gaseous hydrogen fluoride.

[e] Fluoride emissions for the run-of-pile triple superphosphate process are almost entirely silicon tetrafluoride.

[f] The emission factor is for a controlled process using cyclones and primary and secondary scrubbers as control devices.

[g] Coal combustion as a source of HF emissions is discussed in detail in Section 3. The emissions are based on 1974 and 1978 data.

Figure 5-1 shows a typical HF manufacturing operation. The reaction is endothermic and is usually carried out in externally heated horizontal rotary kilns for 30 to 60 minutes at 392°F to 482°F. Dry fluorspar and a slight excess of sulfuric acid are fed continuously to the front end of the kiln. Calcium sulfate or anhydrite is removed at the opposite end. HF, excess sulfuric acid, silicon tetrafluoride, sulfur dioxide, carbon dioxide, and water, produced as primary or secondary reaction products, are removed from the front end of the kiln. HF vapors are condensed in refrigerated condensers and are delivered to an intermediate storage tank. The uncondensed gases are passed through a sulfuric acid absorption tower to remove the remaining HF. Any residual HF in the uncondensed gas stream and the silicon tetrafluoride are recovered as fluosilicic acid in water scrubbers. The collected HF is distilled to a purity of 99.98 percent.[2]

HF emissions to the atmosphere are controlled to a large extent by the condensation and absorption processes involved in HF purification. In addition, a caustic scrubber is used to remove any remaining HF in the process tail gas to an efficiency of greater than 99 percent. Based on data averaged from four HF manufacturing plants, the uncontrolled HF emission factor for the process is 25.0 lbs HF/ton pure acid produced.[2] For these tests, no data on measurement techniques used are available. In 1980, 213 x 10^3 tons HF were produced.[3] Assuming that all the tail gas vents are controlled, this yields a total HF emission rate of 21.3 tons HF/year.

PRIMARY ALUMINUM INDUSTRY

The base ore for primary aluminum production is bauxite, a hydrated oxide of aluminum consisting of 30 to 70 percent alumina (Al_2O_3) and lesser amounts or iron, silicon and titanium. Bauxite ore first is purified to alumina by the Bayer process, and then the alumina is reduced to elemental aluminum. The production of alumina and the reduction of alumina to aluminum are two separate processes and are seldom accomplished at the same location. Fluoride emissions from primary aluminum production are from the reduction process only.[4]

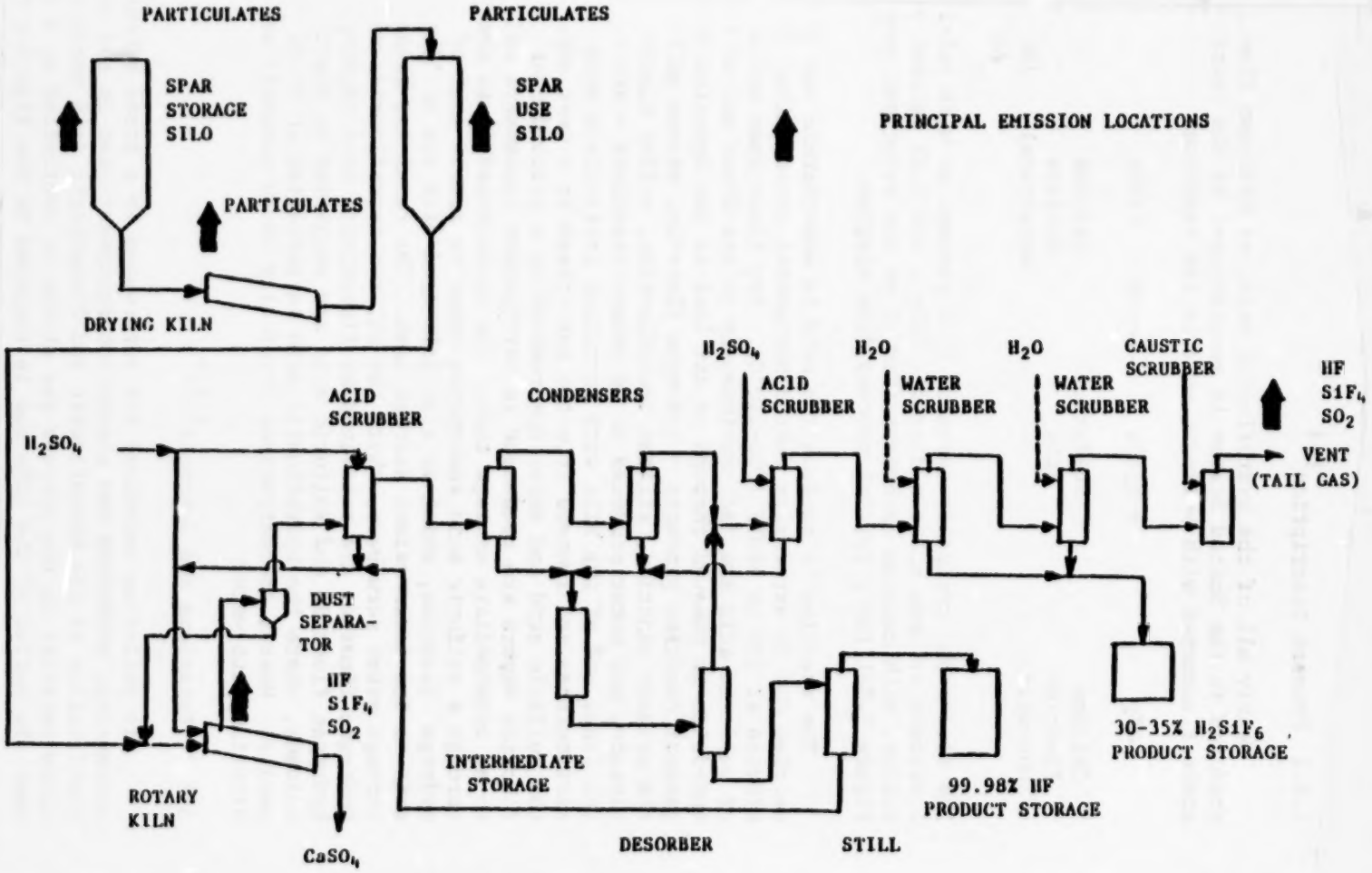

Figure 5-1. Process flow diagram of typical HF plant.[2]

Alumina is reduced to aluminum and oxygen by direct electric current in the Hall-Heroult process, represented below:

$$\underset{\text{Alumina}}{2\,Al_2O_3} \xrightarrow{\text{Electrolysis}} \underset{\text{Aluminum}}{4Al} + \underset{\text{Oxygen}}{3O_2}$$

This reaction is carried out in shallow rectangular cells (pots) made of carbon-lined steel with carbon blocks that are suspended above and extend down into the pot. The pots and carbon blocks serve as cathodes and anodes, respectively, for the electrolytical process.

The pots contain cryolite, a double fluoride salt of sodium and aluminum (Na_3AlF_6), which serves as an electrolyte and a solvent for the alumina. The alumina is dissolved in the molten cryolite bath. The cells operate between 1740°F and 1830°F with heat that results from the resistance between the electrodes. During the reduction process, the aluminum is deposited at the cathode where, because of its heavier weight (142 lbs/ft^3 versus 131 lbs/ft^3), it remains as a molten metal layer underneath the cryolite. The aluminum product is tapped periodically and is fluxed to remove trace impurities. The byproduct oxygen migrates to and combines with the consumable carbon anode to form carbon dioxide and carbon monoxide, which continually evolve from the cell. In a typical plant, a large number of these cells are linked together (electrically in series) to form the basic production unit of the reduction plant.

Aluminum reduction cells are distinguished by the anode configuration used in the pots. Three types of pots are currently used: (1) prebaked (PB), horizontal stud Soderberg (HSS), and (3) vertical stud Soderberg (VSS). The three types of pots are shown in Figures 5-2, 5-3, and 5-4. Most of the aluminum domestically produced is processed in PB cells. These cells use anodes that are press formed from a carbon paste and baked in a direct-fired ring furnace or indirect-fired tunnel kiln. Volatile organic vapors from the coke and pitch paste comprising the anodes are emitted, and most are destroyed in the baking furnace. The baked anodes, typically 14 to 24 per cell, are attached to metal rods and serve as replaceable anodes. Prebaked cells are

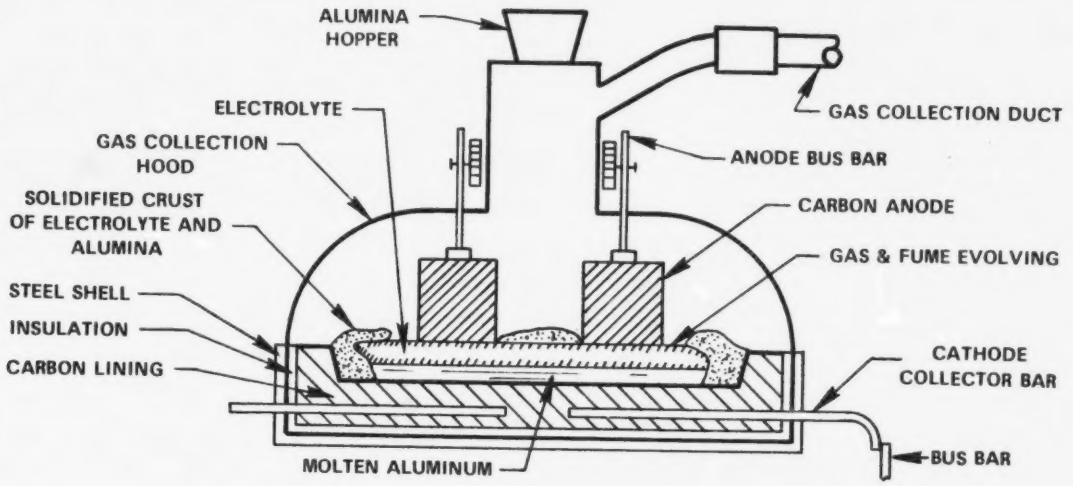

Figure 5-2. Details of prebake reduction cell.[5]

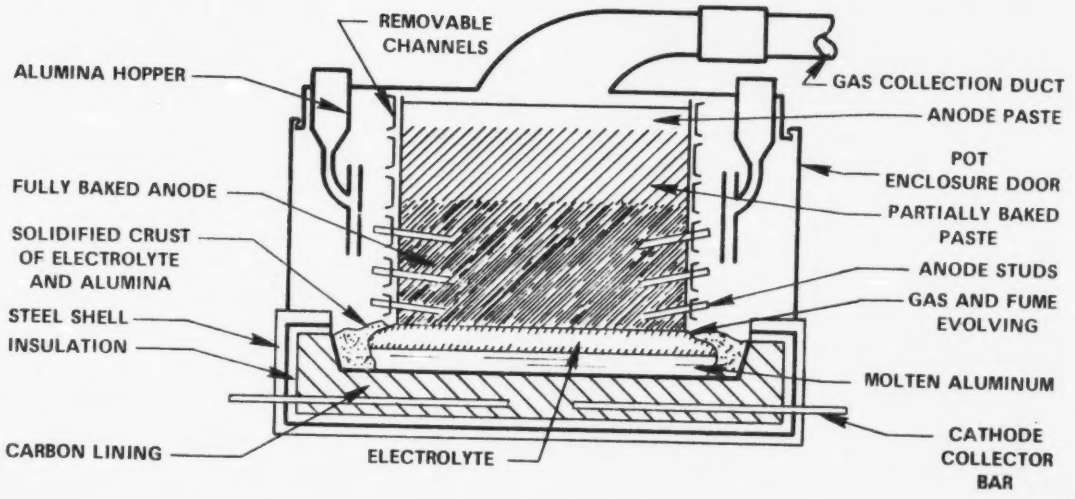

Figure 5-3. Details of horizontal stud Soderberg reduction cell.[5]

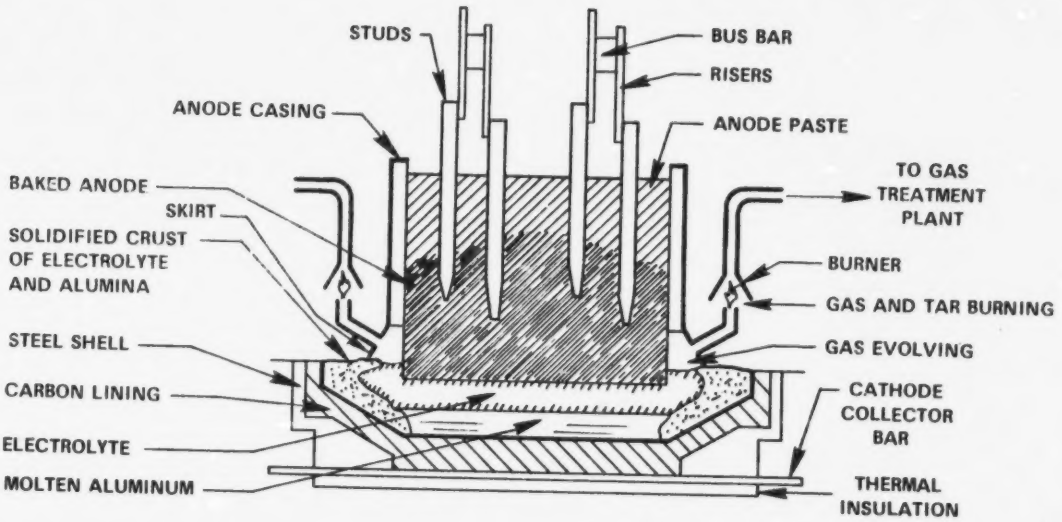

Figure 5-4. Details of vertical stud Soderberg reduction cell.[5]

preferred over Soderberg cells because of their lower power requirements, reduced generation of volatile pitch vapors from the carbon anodes, and provision for better cell hooding to capture emissions.

The second most commonly used reduction cell is the HSS. This cell uses a "continuous" carbon anode. A green anode paste of pitch and coke is added periodically at the top of the super structure and is baked by the heat of the cell to a solid mass as the material moves down the casing. The cell casing consists of aluminum sheeting and perforated steel channels, through which electrode connections or studs are inserted horizontally into the anode paste. During reduction, as the baking anode is lowered, the lower row of studs and the bottom channel are removed, and the flexible electrical connectors are moved to a higher row. Heavy organics from the anode paste contribute to the cell emissions. The heavy tars can cause plugging of ducts, fans, and emission control equipment.

The VSS cell is similar to the HSS cell, except that the studs are mounted vertically in the anode paste. Gases from the VSS cells can be ducted to gas burners and the tars and oils burned. The construction of the VSS cell prevents the installation of an integral gas collection device, and hooding is restricted to a canopy or skirt at the base of the cell where the hot anode enters the cell bath.

The present trend in aluminum production is toward prebake cells. In 1977 the distribution of existing aluminum production capacity by cell type was: center-worked prebake cells at 51 percent of production; side-worked prebake at 16 percent; vertical studs at 13 percent; and horizontal studs at 20 percent. Total production in 1980 was 5,130,000 tons.

Emission Sources and Control Techniques

Fluoride emissions from primary aluminum production occur in the gaseous phase as HF with a small amount of silicon tetrafluoride (SiF_4) and in the particulate phase as cryolite (Na_3ALF_6), aluminum fluoride (AlF_3), calcium fluoride (CaF_2) (fluorspar), and chiolite ($Na_5Al_3F_{14}$). The ratio of gaseous to particulate fluorides varies from 1.2 to 1.7 with PB and HSS cells and is

approximately 3.0 with VSS cells. Particulate emissions of fluorine compounds comprise approximately 10 to 25 percent of the total particulate in primary aluminum production.

The principal points of HF emissions are the primary and secondary emissions from the potrooms housing the reduction cells and, in the case of the prebake cell, the emissions from the associated anode bake plants. Emission factors for gaseous fluoride are presented in Table 5-2 for uncontrolled processes. HF emissions from bauxite grinding and aluminum hydroxide production are negligible. The manufacture of anodes for PB cells emits HF from fluorides in the recycled anode butts and other particulate matter. All three types of reduction cells emit HF from thermal hydrolysis of volatized bath materials, particularly cryolite. The reaction of solid and vaporized fluorides at elevated temperatures occurs primarily at the point where the hot gases escape through vents in the crust at the cell surface. The hydrogen required for the formation of HF is supplied in part from water vapor in the air. Other sources of hydrogen include residual moisture in the alumina and bath raw materials and hydrocarbons in the carbon anodes.

A variety of control devices have been used to abate emissions from reduction cells and anode baking furnaces. To control gaseous and particulate fluorides, one or more types of wet scrubbers (spray tower and chambers, quenchtowers, floating beds, packed beds, venturis, and self induced sprays) have been applied to all three types of reduction cells and to anode baking furnaces. Also particulate control methods such as electrostatic precipitators (wet and dry), multiple cyclones, and dry alumina scrubbers (fluid bed, injected, and coated filter types) have been employed with baking furnaces and with all three cell types.

The control of fluoride emissions from the potroom is dependent on the capture efficiency of the collection systems. Hoods are the most prevalent type of collection system in potrooms. The characteristics of the different cell types place various limitations on hooding design. Center-worked prebake cells can achieve primary capture efficiencies of 95 percent; side-worked prebake cells achieve a primary capture efficiency of only 85 percent or less.[4]

TABLE 5-2. HF EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION PROCESSES[a]

Operation	Emission factor (lbs HF/ton Al)
Anode baking furnace	
Uncontrolled	0.9
Fugitive	NA[b]
Spray tower	0.04
ESP	0.04
Dry alumina scrubber	0.009
Prebake cell	
Uncontrolled	24.0
Fugitive	1.2
Emissions to collector	22.8
Multiple cyclones	22.8
Dry alumina scrubber	0.2
Dry ESP & spray tower	1.4
Spray tower	1.4
Floating bed scrubber	0.5
Coated bag filter dry scrubber	3.4
Cross flow packed bed	6.7
Dry & secondary scrubber	0.4
Vertical Soderberg stud cell	
Uncontrolled	33.0
Fugitive	4.9
Emissions to collector	28.1
Spray tower	0.3
Venturi scrubber	0.3
Multiple cyclones	28.1
Dry alumina scrubber	0.3
Scrubber & wet ESP & spray screen & scrubber	1.5
Horizontal Soderberg stud cell	
Uncontrolled	22.0
Fugitive	2.2
Emissions to collector	19.8
Spray tower	7.5
Floating bed scrubber	0.4
Scrubber & wet ESP	0.2
Wet ESP	1.0
Dry alumina scrubber	0.4

[a]Reference 4.

[b]Information not available.

The HSS cells typically have hood doors that extend the full length of both sides of the cell, achieving total fluoride primary collection efficiencies of 85 to 95 percent. VSS cells typically have a hood skirt, which consists of an inverted U- or V-shaped channel that runs around the edge of the anode for VSS potlines of 75 to 92 percent. The proper approach for all cell types is to seal the hood tightly and to perform as many cell operations as possible with the hood intact. Emissions that are captured within the hood are ducted to a primary control device. Emissions that escape the hooding and are captured at the roof are termed secondary emissions. Ninety-five percent of the domestic primary aluminum production capacity has at least primary control. Eleven percent of the production capacity has best primary control and secondary control.

Primary and secondary fluoride control equipment falls into three classes:

- Dry scrubbing equipment suitable for potroom primary control,
- Wet scrubbing equipment suitable for potroom primary control and anode bake plant control, and
- Wet scrubbing equipment suitable for potroom secondary control.

There are primarily two types of dry scrubbing equipment, fluidized bed and injected alumina. In both processes, the cell gas is contacted with sandy alumina. HF present in the gas is absorbed chemically by the alumina, and virtually all of the cell gas particulate is trapped in the fluid bed. Fugitive particulate matter is caught by a baghouse mounted over the reactor. When the bags are cleaned, the catch drops back into the fluid bed reactor. This system is capable of 98 percent particulate and 99 percent HF removal efficiencies on prebake potline effluents.

Wet scrubbing techniques include the wet electrostatic precipitator (ESP) and the spray tower. In the spray tower, the gas flows countercurrently at low velocity through a device where it is contacted by water, alkaline liquor, or limed water. Spray towers can achieve removal efficiencies for potline HF emissions in percentages ranging in the nineties; however, spray towers show relatively low removal efficiencies for fine particulate. Typical gaseous fluoride removal efficiencies are 95 percent for prebake potlines, 99 percent

for VSS potlines, 93 percent for HSS potlines, and 96 percent for anode bake plant ring furnaces. Electrostatic precipitators fall into two categories: dry ESP's where the collected particulates are knocked off the plates and wires by mechanical rapping to be gathered dry in a hopper; and wet ESP's where the plates and wires are washed with falling water or electrostatically collected mist with the particulates removed as a slurry. Electrostatic precipitators may be designed for almost any selected efficiency. By controlling humidity of the incoming gas and by operating at high voltage, both wet and dry precipitators can achieve 98 to 99 percent removal of potline cell gas particulates. The total fluoride removal efficiencies for scrubber-wet ESP controls vary from 99.2 to 99.9 percent on domestic VSS plants and from 95 to 99 percent on domestic HSS plants.

Secondary control equipment for the potroom is most often a spray screen scrubber. The term spray screen scrubber is applied to wet scrubbing equipment in which the liquor is sprayed into a gas stream and onto screens or open mesh filters enclosed in a plenum chamber. The assembly also usually includes a mist eliminator. The gaseous removal mechanism is absorption into the liquid droplets.

Abnormal Operation

Normal cell operation is interrupted by occasional anode effects, cell working to introduce alumina feed, and periodic tapping of molten aluminum. Cells may also be operated at elevated temperatures in a "sick" condition. At high bath temperatures the bath salts vaporize and are carried into the cell emissions. Normal operating temperatures for cells are between 1780°F and 2000°F. Abnormal or "sick" cells operate at temperatures in excess of 1830°F and sometimes do not crust over. Under these conditions, the high-temperature molten electrolyte is exposed, and there is a large increase in volatilization of bath salts with a corresponding increase of fluoride.

Fluoride Emission Factors[4]

The HF emission factor for PB cells is the sum of the HF emission factors for the anode baking furnace and the PB reduction cell. HF emissions from an anode baking furnace range from 0.009 lbs HF/ton Al, representing uncontrolled

sources. It is estimated that 43 percent of the anode baking furnaces are controlled. The mean of the controlled emission factors is 0.025 lbs HF/ton Al. Fifty-seven percent of the furnaces have uncontrolled emissions with an emission factor of 0.9 lbs HF/ton Al. The weighted average emission factor for anode baking furnaces is 0.52 lbs HF/ton Al.

Prebake cells have controlled emission factors ranging from 0.2 to 6.7 lbs HF/ton Al. The mean controlled emission factor is 2.0 lbs HF/ton Al produced, and 92 percent of the prebake cells have some form of emission control. The total uncontrolled emissions are 24.0 lbs HF/ton Al; 22.8 lbs HF/ton Al are captured and ducted to a primary control device, but the remaining 1.2 lbs HF/ton Al are fugitive emissions with no control. An overall emission factor of 4.9 lbs HF/ton Al represents the weighted average emission factor with consideration of controlled and uncontrolled sources. Coupled with the emissions from the anode baking furnace, prebake reduction cells have an overall emission factor of 5.4 lbs HF/ton Al.

The HF emission factor for VSS cells is 0.6 lbs HF/ton Al. The mean emission factor for HSS cells is 1.9 lbs HF/ton Al. All VSS and HSS cells have at least primary emission control devices and uncontrolled fugitive emissions. This leads to an overall emission factor for VSS cells of 5.5 lbs HF/ton Al and 4.1 lbs HF/ton Al for HSS cells.

Table 5-3 provides a summary of the emission factors for various cell types and the associated nationwide HF emissions from aluminum production.

PHOSPHATE FERTILIZER INDUSTRY

The phosphate fertilizer industry is a segment of the agricultural chemical industry involved in the production and marketing of nutrient commodities for crop production. The phosphate fertilizer industry begins with the mining of phosphate rock; proceeds with the basic chemical production of phosphoric acid and its subsequent processing to diammonium phosphate (DAP), superphosphoric acid (SPA), and triple superphosphate (TSP); and culminates in fertilizer blending for consumer use. Figure 5-5 provides a summary of the major phosphate rock processing steps.[6]

TABLE 5-3. SUMMARY OF OVERALL HF EMISSION FACTORS AND NATIONWIDE EMISSIONS FROM PRIMARY ALUMINUM PRODUCTION

Cell type[a]	Emission factor (lbs HF/ton Al)	Nationwide emission (10^3 tons HF/yr)
Prebake cells (PB)	5.4	9.3
Vertical Soderberg cells (VSS)	5.5	1.8
Horizontal Soderberg cells (HSS)	4.1	2.2
Total		13.3

[a]1977 distribution by cell type was: PB 67%; VSS 13%; and HSS 20%.

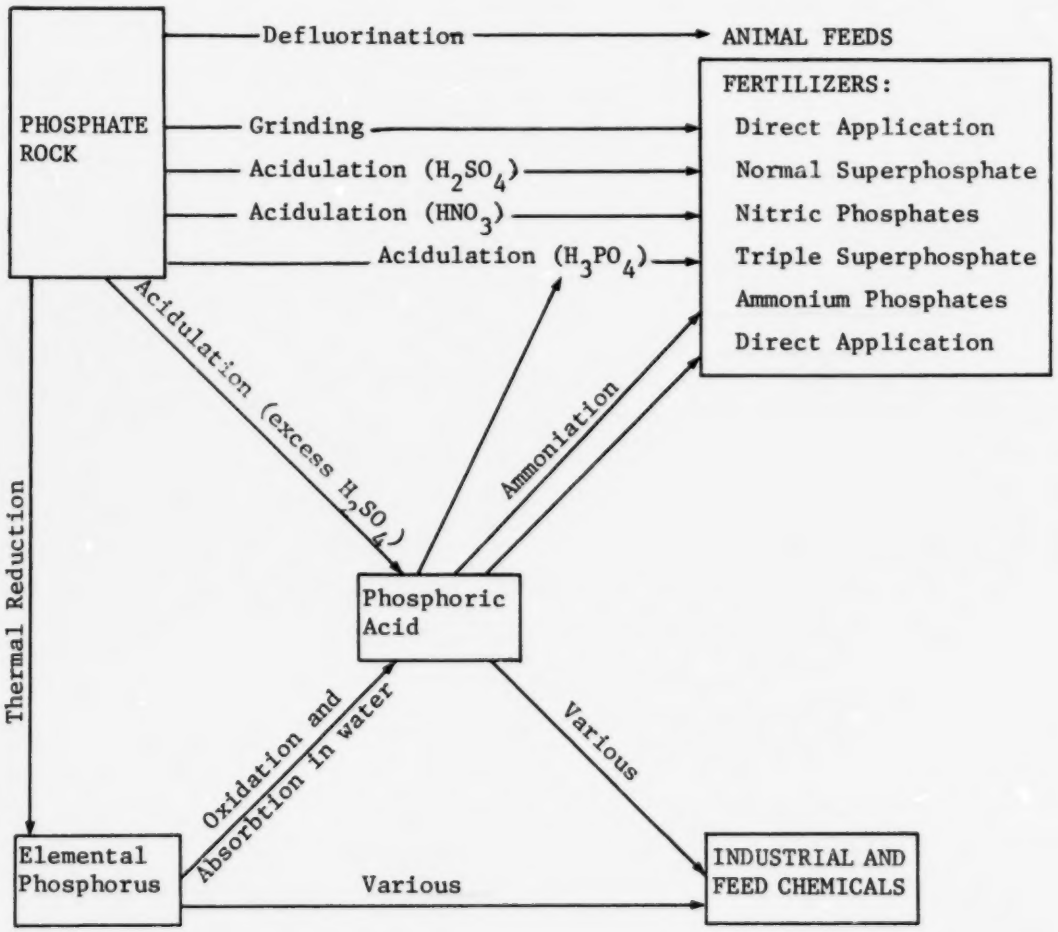

Figure 5-5. Major phosphate rock processing steps.

Phosphoric Acid Production

Phosphoric acid is an intermediate product in the manufacture of phosphate fertilizers. Phosphoric acid is produced by two principal methods, the wet process and the thermal process. The wet process is used when the acid is to be used for fertilizer. The wet process emits the gaseous fluorides, primarily HF, since phosphate rock contains 3.5 to 4.0 percent fluorine.[7]

The overall reaction in the wet process is described by the following reaction:

$$CaF_2 \cdot 3Ca_3(PO_4) + 10\ H_2SO_4 + 20\ H_2O \longrightarrow$$
$$10\ CaSO_4 \cdot 2\ H_2O + 2\ HF + 6\ H_3PO_4$$

In the actual process, finely-ground phosphate rock is fed continuously into the reactor, and sulfuric acid is added. Gypsum crystals ($CaSO_4 \cdot H_2O$) are precipitated by the acid and phosphate rock reaction. Because the proper ratio of acid to rock must be maintained as closely as possible, these two feed streams are controlled automatically. Several different reactor designs are available to accomplish the phosphate rock digestion. Each reactor type, however, provides an environment that leads to digestion of the rock and proper formation of gypsum crystals.

The reaction slurry is held in the reactor for up to 8 hours and is filtered. This produces a 32 percent acid solution, which generally needs concentrating for further use. Current practice is to evaporate it in vacuum evaporators to approximately 54 percent phosphorus pentoxide (P_2O_5). Figure 5-6 shows the overall phosphoric acid manufacturing process.[7]

Of the fluorine contained originally in the phosphate rock, after digestion, some is precipitated with the gypsum, some goes with the phosphoric acid product, and the rest vaporizes in the reactor. The actual distribution of fluorine compounds depends upon the type of rock treated, process used, and operating conditions. In the following discussion of fluoride emissions, it is assumed that gaseous fluoride emissions are in the form of hydrogen fluoride.

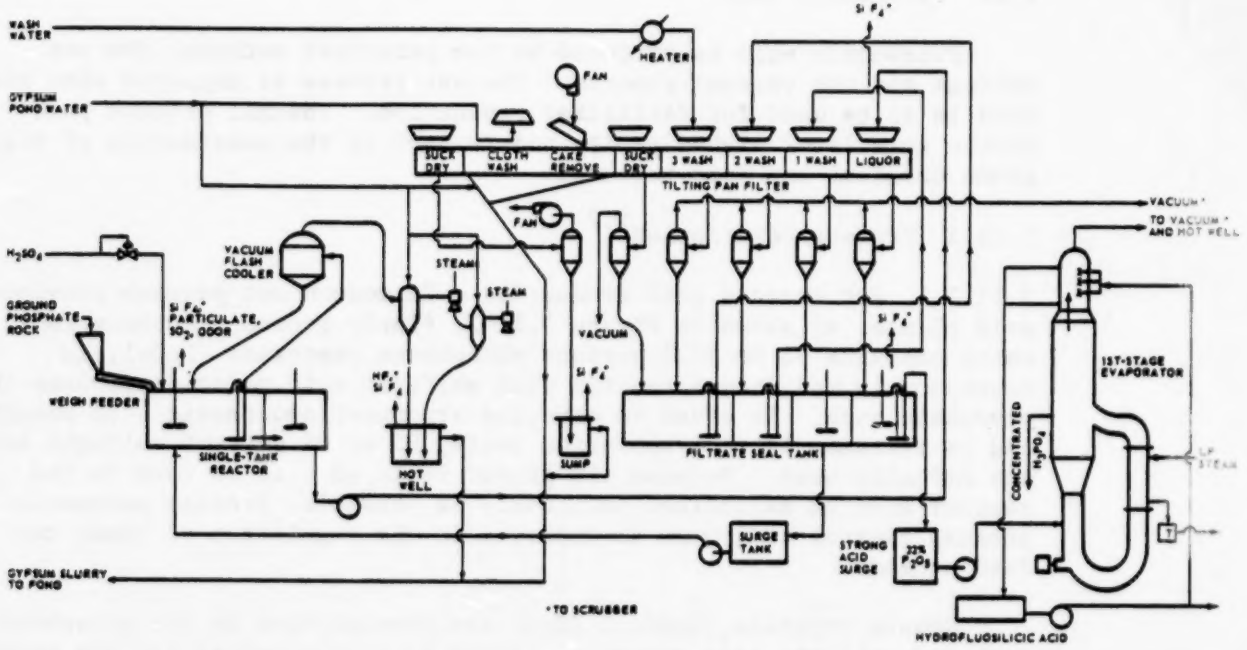

Figure 5-6. Flow diagram of wet process phosphoric acid plant.[7]

The reactor is the major source of fluoride emissions from the process. Additional sources are the filter, the filtrate feed and seal tanks, the flash coolers seal tank, the evaporator system hotwell, and the acid storage tank. The primary reactor emission source is the reactor tank, where HF is evolved during digestion of the phosphate rock. To prevent an excessive temperature rise in the reactor, the heat of reaction is removed by cycling a portion of the reaction slurry through a vacuum flash cooler. Vapors from the cooler are condensed in a barometric condenser and sent to a hot well, while the non-condensibles are removed by a steam ejector and vented to the hot well. The majority of HF evolved in the flash cooler is absorbed by the cooling water in the barometric condenser. The uncontrolled emission factor for the reactor is estimated to range from 0.04 to 2.2 lbs HF/ton P_2O_5 produced,[6] with a mean of 1.12 lbs HF/ton P_2O_5.

The filter is the second largest source of fluoride emissions. Most of the HF is evolved at the points where feed acid and wash liquor are introduced to the filter. These emission factors range from 0.01 to 0.06 lbs HF/ton P_2O_5,[6] with a mean of 0.035 lbs HF/ton P_2O_5 or 0.012 lbs HF/ton phosphate rock processed.

The third source of HF emissions is the multiple effect evaporator used to concentrate the phosphoric acid product. Most HF in this step is collected in the system's barometric condensers; the remaining HF, however, exits with the non-condensibles and is released to the atmosphere from the hot wells. Up to 0.26 lbs HF/ton P_2O_5 or an average of 0.043 lbs HF/ton rock processed may be released to the atmosphere from the hot wells and other minor sources.[6]

For the entire process, the average uncontrolled emission factor is 0.425 lbs HF/ton phosphate rock processed. As a result of control by scrubbers, it is estimated that a typical emission factor of approximately 0.03 lbs HF/ton P_2O_5 or 0.01 lbs HF/ton phosphate rock processed can be used to represent HF emissions from phosphoric acid production. This estimate is based on the fact that all wet-process acid plants located in Florida (the major phosphate rock producing state) are required to meet an emission level of 0.02 lbs of total fluoride/ton P_2O_5. It is estimated that 74 percent of production is in attainment with the 0.02 level. The remaining 26 percent ranges from 0.02 to 0.07 lbs of total fluoride/ton P_2O_5. Also, all wet

process plants built since 1967 are assumed to have installed spray-crossflow packed bed scrubbers. With a 1980 wet process phosphoric acid production of approximately 10×10^6 tons/year,[8] total HF emissions would be 150 tons/year.

Gypsum Ponds

As described above, a wet process phosphoric acid plant produces gypsum in a slurry. In addition, the scrubber and condenser water used in the acid manufacturing process must be disposed of. Large storage ponds, known as gypsum ponds, are used for disposal. Also, if the same plant produces DAP or TSP, spent scrubbing water also may be disposed of in the gypsum ponds. Since both gypsum and scrubbing and condenser water contain fluorides, primarily HF, the gypsum pond can be a large source of HF emissions.

HF emission factors have been estimated at 0.2 to 10 lbs fluorides/acre-day measured as HF due to volatilization of HF from the ponds. The emission factor depends both on the HF concentration in the pond and on the wind velocity and other ambient conditions. Based on wet phosphoric acid production, plants have gypsum ponds in the range of 0.1 to 0.4 acres per daily ton of acid.[9] An average emission factor based on an HF emission factor of 5.1 lbs HF/acre-day representing average wind and temperature conditions and on 0.25 acres (pond size) per daily ton of acid would be 1.275 lb HF/ton acid produced[9] or 0.42 lbs HF/ton phosphate rock processed (based on 0.333 tons P_2O_5/ton phosphate rock). This emission factor should be considered as a rough estimate because of the difficulties involved in emission measurement from a pond. Based on total acid production in 1980 of $10{,}000 \times 10^3$ tons/year,[8] 6400 tons HF would be emitted annually.

Triple Superphosphate Manufacture

Triple superphosphate is a product obtained by treating phosphate rock with phosphoric acid. According to the grade of rock and the strength of acid used, the product contains from 44 to 47 percent available P_2O_5. In the

manufacturing operation, phosphoric acid containing 52 to 54 percent P_2O_5 is mixed at ambient temperatures with ground phosphate rock. The reaction that occurs is represented by the following equations:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10\ H_2O \longrightarrow 10\ CaH_4(PO_4)_2 \cdot H_2O + 2\ HF$$

After mixing, the slurry is directed to a "den" where solidification occurs. The solidified slurry which exits from the den must be cured for 3 or more weeks to allow the reactions to approach completion. The finished product then is sent to storage.

Fluoride emissions from storage and production areas at "run-of-pile" triple superphosphate plants range from 31 to 48 lbs/ton of P_2O_5 input; however, silicon tetrafluoride is the only fluoride released in appreciable quantities.[10]

The major sources of fluoride emissions from a granular triple superphosphate plant are the reactors, den, granulator, dryer and cooler.[11] Uncontrolled emissions from these sources have been estimated at a rate of 21 lbs F/ton P_2O_5 input.[10] A controlled emission factor of 0.24 lbs F/ton P_2O_5 input from granulator plants is reported.[11] Assuming that most of the fluorides are emitted in the form of hydrogen fluoride results in uncontrolled and controlled emission factors of 21 and 0.24 lbs HF/ton P_2O_5 input, respectively. For the 1980 production of triple superphosphate of 1.693×10^3 tons as P_2O_5,[8] 0.21 tons of HF would be emitted based on the controlled factor.

Diammonium Phosphate Manufacture

Diammonium phosphate is obtained by the reaction of ammonia with phosphoric acid according to the following reaction:

$$2\ NH_3 + H_3PO_4 \longrightarrow (NH_4)_2HPO_4$$

Air emissions from production of ammonium phosphate fertilizer result from five process operations. The reactor and ammoniator granulator produce emissions of gaseous ammonia, gaseous fluorides (HF), and particulate ammonium

phosphates. Exhaust gases from the dryer and cooler also contain ammonia, fluorides, and particulate matter; these streams are combined and passed through cyclones and primary and secondary scrubbers. Uncontrolled emissions from the dryer and coolers and from the ammoniator/granulator are each 0.3 lbs F/ton P_2O_5.[12] Controlled emissions of 0.08 lbs F/ton fertilizer have been reported.[13] Assuming that most of the fluorides are emitted as HF results in uncontrolled and controlled emission factors of 0.3 and 0.008 lbs HF/ton P_2O_5 input, respectively. Based on the controlled factor and the 1980 production of 6.125×10^3 tons of diammonium phosphate,[8] 245 tons HF would be emitted.

REFERENCES

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4. Primary Aluminum Production. In: AP-42, Environmental Protection Agency, Research Triangle Park, NC, April 1981. pp. 7.1-1 to 7.1-8.

5. Primary Aluminum: Guidelines for Control of Fluoride Emissions from Existing Primary Aluminum Plants. EPA-450/2-78-049b, U.S. Environmental Protection Agency, Office of Air, Noise, and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC. December 1979.

6. Final Guideline Document: Control of Fluoride Emissions From Existing Phosphate Fertilizer Plants. EPA-450/2-77-005, U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, NC, March 1977.

7. Phosphoric Acid. In: AP-42, Environmental Protection Agency, Research Triangle Park, NC, February 1980. pp. 5.11-1 to 5.11-5.

8. Fertilizer Outlook and Situation. U.S. Department of Agriculture, Washington, DC, December 1982. p. 8.

9. Reference 6, pp. 5-15 to 5-16.

10. Reference 6, pp. 5-10 to 5-11.

11. Triple Superphosphates. In: AP-42, Environmental Protection Agency, Research Triangle Park, NC, October 1980. pp. 6.10.2-1 to 6.10.2-5.

12. Reference 6, p. 5-9.

13. Ammonium Phosphates. In: AP-42, Environmental Protection Agency, Research Triangle Park, NC, October 1980. pp. 6.10.3-1 to 6.10.3-4.

APPENDIX A

ACCURACY ASSESSMENT OF EMISSION FACTORS

INTRODUCTION

This Appendix addresses the accuracy and applicability of the emission factors for HCl and HF presented in Sections 3 through 5 of this report. This work was conducted primarily under EPA Contract 68-02-3698, Task No. 2, and, subsequently was adapted for inclusion in this report. The original report was prepared by Sean O'Brien, Tom Sylvia, Bob Kane and Mark Gollands of GCA/Technology Division for the Air and Energy Engineering Research Laboratory. Merrill Jackson was the EPA Project Officer.

The purpose of this evaluation is to provide a qualitative indication of the reliability of the emission factors. The information presented here could be used by future NAPAP or other workers in two ways. Qualitative rankings can be used as preliminary inputs for uncertainty analyses such as those currently underway for sulfur and nitorogen oxides. Secondly, as the sophistication of the Eulerian modeling effort increases, the accuracy requirements for emission factors for certain sources may become more stringent. The assessments provided in this Appendix could be used to prioritize additional data gathering.

CRITERIA FOR ASSESSING EMISSION FACTORS

The criteria listed below were established to assess the accuracy of the emission factors.

- Test methods used: Most emission factors are determined from either source tests, industry surveys, mass balances, or engineering estimates. The accuracy of these methods is dependent on several different parameters which change from one emission source to another.

- Source Test: In source testing, samples are taken directly from the source emitting the pollutant. Accurate approved test methods should have been used whenever possible. If an unapproved method or an outdated method was used the accuracy of the emission factor should be questioned.

- Industry Survey: In a survey EPA sumbits a series of questions to a plant or site that is emitting the pollutant in question. They voluntarily fill out and return the questionnaire to the surveyor. To obtain accurate information the questions must be worded carefully so that the correct and desired information will be given. If consistent results are reported by the participants, the information may be considered accurate. To effectively assess the accuracy of an emission factor, the survey methodology should be known.

- Engineering Estimate: An engineering estimate is based on process information available to the engineer. The engineer makes several assumptions based on his experience and knowledge of the process. Using these assumptions and other available information he estimates an emission factor. This method of determining an emission factor is generally the most inaccurate. However, with adequate background information, frequently an accurate estimate can be made.

- Size of Data Base: The emission factor becomes increasingly accurate as the data base from which the factor was determined expands. Emission factors constructed on information from one source have less credibility than those from several sources.

- Data Base Represents a Good Cross Section of Industry: An average emission factor should be determined from a cross section of the industry. A good cross section is related to the size of the data base. However, a large data base does not insure a good cross section, and an excellent cross section is possible from a small data base.

- Age of Data: For the following reasons some emission factors quickly lose credibility:

  - The sampling and testing methods may have been proven invalid and as better methods are developed, inherent flaws in previously used methods are discovered.

  - Innovations in technology occur in most industries on a regular basis. Consequently, the process parameters used when the emission tests were performed may differ significantly from what is currently used in the industry. Control systems may be more efficient, fuel feed and production rates may differ, the composition of pollutants may be significantly different, etc. As a result, the old emission factor may no longer apply.

- New laws and regulations may be passed which would significantly affect the emissions from a source.

RATING SYSTEM

A ranking system, analogous to the AP-42 system, was developed to grade each emission factor. Due to the variability in the type of information contained in the reference used to assign emission factors, a good deal of subjective engineering judgment was used in giving each factor a grade.

Emission factors for each process were given a ranking of A through E, a ranking of A representing the more accurate emission factor and a ranking of E the least.

A qualitative description of each rank is as follows:

- A
  - Large data base from surveys or source tests on several different studies was used.
  - Data base covers a good cross section of the industry.
  - Emissions were measured using currently valid test methods.
  - Emission factors were determined by mass balance based on sound measurement.
- B
  - Data base is fairly large, however, it is not clear that it represents a good cross section of the industry.
  - Emission factor was measured using valid test methods at the time the test was performed. However, tests have since been revised.
  - Engineering estimate based on sound accurate information
- C
  - Data base consists of a few good sources.
  - Data may or may not be representative of the industry.
  - Engineering estimates based on accurate information. However, information is not extensive or complete.

- D
  - Data base is small. If one sample, it was a representative site.
  - Data base may not be representative of industry.
  - Unapproved test methods may have been used.
  - Engineering estimates are based on information where accuracy is questionable.
- E
  - Data base is small. Results conflict with each other.
  - Any sources tested are not representative of the industry.
  - Engineering estimates are based on very little reliable information.

RESULTS FORMAT

In the following subsection, the accuracy assessment is presented. Each listing contains the following:

- Source title;
- Emission factor using SCC units;
- Accuracy ranking;
- Brief description of how emission factors were derived; and
- References where information was found.

ACCURACY OF HYDROGEN CHLORIDE EMISSION FACTORS

Table A-1 summarizes the hydrogen chloride (HCl) emission factors and accuracy rankings for the major source categories.

TABLE A-1. HYDROGEN CHLORIDE EMISSION FACTORS AND ACCURACY RANKINGS

Coal Combustion Utility Boilers

Emission Factor: 78.8 lbs/10^9 Btu bituminous

Ranking: B

Emission Factor: 1.0 lbs/10^9 Btu lignite

Ranking: B

Emission Factor: 35.5 lbs/10^9 Btu anthracite

Ranking: C

Emission factors for butiminous and lignite coal were determined from a study by TRW and GCA of 46 sites from several parts of the country. Measurements were made using an EPA SASS train. The emission factor for anthracite coal was calculated from trace element concentrations data.

Reference

1. Shih, C.C. et al. Emissions Assessment of Conventional Stationary Combustion Systems: Volume III. Electricity Generation External Combustion Sources. EPA-600/7-81-003a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1981.

Coal Combustion Industrial Boilers

Emission Factor: 78.8 lbs/10^9 Btu bituminous

Ranking: B

Emission Factor: 1.0 lbs/10^9 Btu lignite

Ranking: B

Emission Factor: 35.5 lbs/10^9 Btu anthracite

Ranking: C

Emission factors for bituminous and lignite coal were determined from a study by TRW and GCA of 32 sites from several parts of the country. Measurements were made using an EPA SASS train. The emission factor for anthracite coal was calculated from trace element concentrations data.

(continued)

Reference

1. Surprenant, N.F. et al. Emissions Assessment of Conventional Stationary Systems: Volume V. Industrial Combustion Sources. EPA-600/7-81-003c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1981.

Coal Combustion in Residential Boilers

Emission Factors: 120 lbs/10^9 Btu anthracite
60.5 lbs/10^9 Btu bituminous
35.1 lbs/10^9 Btu lignite

Ranking: C

Emission factors were based on data from 1974. Residential boilers represent a small fraction of total coal combustion. Consequently, not many studies have been done.

Reference

1. De Angelis, D.G. and R.B. Reznik, Source Assessments: Residential Combustion of Coal. EPA-600/2-79-019a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1979.

Propylene Oxide Manufacture

Emission Factor: 7.46 lbs/ton product

Ranking: C

Emission factor was derived from a study by Monsanto Research Corp. of four representative Propylene Oxide plants. A standard EPA Chlorine/Chloride Sampling Train was used. Chlorine/chloride emissions are assumed to be mostly in the form of HCl.

Reference

1. Source Assessment: Chlorinated Hydrocarbon Manufacture. EPA-600/2-79-019g, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1970.

(continued)

TABLE A-1. (continued)

Incineration

Emission Factors: Municipal Wastes -- 5 lbs/ton
Industrial Waste -- 5.35 lbs/ton
Liquid Wastes -- 1.19 lbs/ton

Ranking: E

The emission factors were derived from test data from three municipally owned incinerators.

References

1. Chlorine and Hydrogen Chloride. EPA-600/1-76-020, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1976. p. 278.

2. Source Category Survey: Industrial Incinerators. EPA-450/3-80-013, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1980. pp. 5-5 and 5-20.

By-product Hydrochloric Acid Production

Emission Factors: without final scrubber -- 3.0 lbs/ton
with final scrubber -- 0.2 lbs/ton

Ranking: B

Emission factors are based on measurements of 26 plants in 1969. The data have significant scatter.

Reference

1. Hydrochloric Acid. In: AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, Feburary 1972. p. 5.7-1.

Coal combustion accounts for over 85 percent of total hydrogen chloride (HCl) emissions and consequently a great deal of testing has been done in this area. Other sources such as hydrogen chloride manufacture and incineration of industrial wastes account for a much smaller percentage of overall HCl emissions and therefore have undergone less testing.

Emission factors for coal combustion were assigned a high ranking due to the number of tests conducted in this area, the availability of information concerning accuracy, and type of test methods used. The emission factor for propylene oxide manufacture also received a high ranking due to a study conducted by Monsanto Research Co. for this process. In this study, a representative plant was defined for each type of manufacturing process to obtain an accurate depiction of overall emissions from this source. Moreover, this process is essentially uniform in terms of design and control technology so that the emission factor derived from this study is most likely a true representative of emissions from all propylene oxide manufacturing processes. Other sources such as hydrochloric acid manufacturing and industrial waste incineration received intermediate to poor rankings because of the small number of plants actually tested, the absence of information concerning test methodology, and the number of emission factors actually supplied by the acid producers themselves.

ACCURACY OF HYDROGEN FLUORIDE EMISSION FACTORS

Table A-2 summarizes the emission factors and accuracy rankings for the major anthropogenic sources of hydrogen fluoride (HF).

Since coal combustion accounts for the largest source of HF emissions, emissions from this source have received the most in-depth studies. Other sources such as the phosphate fertilizer industry, the primary aluminum industry, and hydrogen fluoride manufacturing represent a significantly smaller fraction of overall HF emissions and consequently have received very few, if any, detailed studies.

Emission factors from all the major coal combustion processes were deemed to be accurate representations of overall emissions from these sources based upon the number of studies completed, availability of information concerning accuracy of test methods, and the representative number of sources tested.

Emission factors from all other sources listed in Table A-2 were assigned very low rankings based upon the low number of studies, absence of information concerning accuracy of test methods, and the number of assumptions made in determining these factors.

TABLE A-2. HYDROGEN FLUORIDE EMISSIONS FACTORS AND ACCURACY RANKINGS

Coal Combustion Utility Boilers

Emission Factor: 9.4 lbs/10^9 Btu bituminous

Ranking: B

Emission Factor: 1.2 lbs/10^9 Btu lignite

Ranking: B

Emission Factor: 7.2 lbs/10^9 Btu anthracite

Ranking: C

Emission factors for bituminous and lignite coal were determined from a study by TRW and GCA at 46 sites in different parts of the country. An EPA SASS train was used. The emission factor for anthracite coal was calculated from trace element concentrations data.

Reference

1. Shih, C.C., et al., Emissions Assessment of Conventional Stationary Combustion Systems: Volume III. Electricity Generation External Combustion Sources. EPA-600/7-81-003a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1981.

Coal Combustion Industrial Boilers

Emission Factor: 9.4 lbs/10^9 Btu bituminous

Ranking: B

Emission Factor: 1.2 lbs/10^9 Btu lignite

Ranking: B

Emission Factor: 7.2 lbs/10^9 Btu anthracite

Ranking: C

Emission factors for bituminous and lignite coal were determined from a study by TRW and GCA at 32 sites in different parts of the country. An EPA SASS train was used. The emission factor for anthracite coal was calculated from trace element concentrations data.

(continued)

TABLE A-2. (continued)

Reference

1. Surprenant, N.F. et al. Emissions Assessment of Conventional Stationary Combustion Systems: Volume V. Industrial Combustion Sources. EPA-600/7-81-003c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1981.

Coal Combustion Residential Boilers

Emission Factors: 4.95 lbs/10^9 Btu anthracite
6.87 lbs/10^9 Btu bituminous
6.34 lbs/10^9 Btu lignite

Ranking: C

Emission factors are based on data from 1974. Residential boilers represent a small fraction of total coal combustion. Consequently, not many studies have been done.

Reference

1. De Angelis, D.G. and R.B. Reznik. Source Assessment: Residential Combustion of Coal. EPA-600/2-79-019a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1979.

Hydrogen Fluoride Manufacture

Emission Factors: Uncontrolled -- 25.0 lb/ton HF produced
Controlled -- 0.2 lb/ton HF produced

Ranking: D

Emission factor came from a study of 4 manufacturing plants. However, very little is known about these tests and their accuracies.

(continued)

TABLE A-2. (continued)

Reference

1. Hydrofluoric Acid: In: AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1980, pp. 5.8-1 to 5.8-4.

Phosphate Fertilizer Industry--Phosphoric Acid Production

Emission Factors: Reactor -- 0.37 lbs/ton phosphate rock
Condenser -- 0.043 lbs/ton phosphate rock
Controlled Emissions -- 0.010 lbs/ton phosphate rock

Ranking: B

Ten sites representing 48% of wet phosphoric acid production in the U.S. were sampled between 1966 and 1967.

Reference

1. Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. Environmental Protection Agency, Office of Air and Waste Management, Research Triangle Park, North Carolina, March 1977.

Phosphate Fertilizer Industry--Gypsum Ponds

Emission Factors 1.275 lbs/ton phosphoric

Ranking: D

Emission factor was based on measurements from two different ponds in Florida. Difficulties are encountered measuring emissions from an open source such as a gypsum pond.

(continued)

TABLE A-2. (continued)

Triple Super-Phosphate Manufacture (Granulor)

Emission Factors: Reactor/dryer -- 21.0 lb/ton P_2O_5
Controlled emissions -- 0.24 lb/ton P_2O_5

Ranking: E

Reference

1. Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. Environmental Protection Agency, Office of Air and Waste Management, Research Triangle Park, North Carolina, March 1977.

2. Triple Superphosphates. In: AP-42, Environmental Protection Agency, Research Triangle Park, North Carolina, October 1980. p. 6.10.2-1.

Diammonium Phosphate Manufacture

Emission Factors: Dryer and coolers -- 0.3 lbs/ton fertilizer
Ammoniation/granulator -- 0.3 lbs/ton fertilizer
Controlled emissions -- 0.08 lbs/ton fertilizer

Ranking: A

Emission factors were determined from "several" sites in Florida.

References

1. Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. Environmental Protection Agency, Office of Air and Waste Management, Research Triangle Park, North Carolina, March 1977.

2. Ammonium Phosphates. In: AP-42, Environmental Protection Agency, Research Triangle Park, North Carolina, October 1980. pp. 6.10.3-1 to 6.10.3-4.

(continued)

TABLE A-2. (continued)

Primary Aluminum Industry

Emission Factors (lbs HF ton Aluminum produced):

Anode baking furnace	0.52
Prebaked reduction cell	4.9
Prebaked fugitive emissions	1.2
Vertical Soderberg stud cells	0.6
VSS--fugitive emissions	4.9
Horizontal Soderberg cells	1.9
HSS--fugitive emissions	2.2

Ranking: A

The emission factors were based on several tests utilizing EPA-approved test methods.

References

1. Primary Aluminum Production: In: AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1981. pp. 7.1-1 to 7.1-8.